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Control of Volatile Organic Compound Emissions from Air Oxidation Processes in Synthetic Organic Chemical Manufacturing Industry

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Control Techniques Guidelines (CTG) are issued for volatile organic compound (VOC) emissions from air oxidation processes within the synthetic organic chemical manufacturing industry. The document informs Regional, State, and local air pollution control agencies of reasonably available control technology (RACT) for development of regulations necessary to attain the national ambient air quality standards for ozone.

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Control of Volatile Organic Compound Emissions from Air Oxidation Processes in Synthetic Organic Chemical Manufacturing Industry

Emission Standards and Engineering Division

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Air and Radiation
Office of Air Quality Planning and Standards
Research Triangle Park, NC 27711

December 1984

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1. INTRODUCTION

The Clean Air Act Amendments of 1977 require each State in which there are areas in which the national ambient air quality standards (NAAQS) are exceeded to adopt and submit revised State Implementation Plans (SIP's) to EPA. Revised SIP's were required to be submitted to EPA by January 1, 1979. States which were unable to demonstrate attainment with the national ambient air quality standards (NAAQS) for ozone by the statutory deadline of December 31, 1982, could request extensions for attaining the standard. States granted such an extension are required to submit a further revised SIP by July 1, 1982.

Both the July 1, 1982, date for submittal of SIP revisions for "extension areas" and the December 31, 1982, deadline for attainment for "nonextension areas" have passed. Nevertheless, certain areas will still be required to adopt reasonably available control technology (RACT) regulations after these dates for volatile organic compound (VOC) source categories when EPA published a control techniques guideline (CTG). Specifically, two types of nonattainment areas are affected: (1) those granted an extension up to 1987 for ozone attainment since schedules for adopting these measures are incorporated in the plan approvals, and (2) those failing to attain by 1982 (as originally projected).[1]

Section 172(a)(2) and (b)(3) of the Clean Air Act require that nonattainment area SIP's include RACT requirements for stationary sources. As explained in the "General Preamble for Proposed Rulemaking on Approval of State Implementation Plan Revisions for Nonattainment Areas," (44 FR 20372, April 4, 1979) for ozone SIP's, EPA permitted States to defer the adoption of RACT regulations on a category of stationary sources of VOC until after EPA published a CTG for that VOC source category. See also 44 FR 53761 (September 17, 1979) and 46 FR 7182 (January 22, 1981). This delay allowed the States to make more technically sound decisions regarding the application of RACT.

Although CTG documents review existing information and data concerning the technology and cost of various control techniques to reduce emissions, they are, of necessity, general in nature and do not fully account for variations within a stationary source category. Consequently, the purpose of CTG documents is to provide State and local air pollution control agencies with an initial information base for proceeding with their own assessment of RACT for specific stationary sources.

1.1 REFERENCES FOR CHAPTER 1

1. "Guidance Document for Correction of Part D SIP's for Nonattainment Areas," Office of Air Quality Planning and Standards, Research Triangle Park, North Carolina, January 27, 1984.

2. THE AIR OXIDATION INDUSTRY

2.1 GENERAL

The unit process of oxidation of organic compounds generally means the chemical reaction with an oxidizing agent to introduce one or more oxygen atoms into the compound, or to remove hydrogen or carbon atoms from the compound, or a combination of the above. This analysis deals with the subset of the oxidation industry in which air, or air enriched with oxygen, is the oxidizing agent.

This chapter describes the air oxidation industry structure, its production processes, and the associated emissions. The air oxidation industry consists of those facilities that produce chemicals included in the synthetic organic chemical manufacturing industry (SOCMI) by reacting one or more chemicals with oxygen supplied as air. This industry also includes chemicals produced using a combination of ammonia and air or of halogens and air as reactants. Processes that use pure oxygen as the reactant or that use an oxidizing agent other than oxygen are not considered in this study.

2.2 INDUSTRY STRUCTURE

It is difficult to separate the chemicals produced in air oxidation processes from other SOCMI products since air oxidation is not the only process to produce some of these chemicals.[1] Several commercial routes exist for many of these air oxidation chemicals including variations in organic feed, oxygen oxidation, or chemical oxidation. Also, many air oxidation chemicals are produced as intermediates for the manufacture of other chemicals. This section discusses the identification of the air oxidation chemicals, their uses and growth, and their domestic production.

2.2.1 Air Oxidation Chemicals

Table 2-1 lists these air oxidation chemicals; however, this list is not exclusive.

Each air oxidation chemical belongs to one of the following general chemical groups:

1. Acid anhydrides,
2. Alcohols,
3. Aldehydes,
4. Alkenes,
5. Carboxylic acids,
6. Esters,
7. Ketones,
8. Nitriles,
9. Oxides,
10. Peroxides, or
11. Halogenated alkanes.

Of the 36 air oxidation chemicals identified, 11 are carboxylic acids. The remaining 25 chemicals include five ketones, five aldehydes, two alcohols, two acid anhydrides, three alkenes, three nitriles, two oxides, one ester, one peroxide, and one halogenated alkane.

TABLE 2-1. SOCMI CHEMICALS PRODUCED BY AIR OXIDATION

1. Acetaldehyde
2. Acetic Acid
3. Acetone
4. Acetonitrile
5. Acetophenone
6. Acrolein
7. Acrylic Acid
8. Acrylonitrile
9. Anthraquinone
10. Benzaldehyde
11. Benzoic Acid
12. 1,3-Butadiene
13. p-t-Butyl Benzoic Acid
14. n-Butyric Acid
15. Crotonic Acid
16. Cumene Hydroperoxide
17. Cyclohexanol
18. Cyclohexanone
19. 1,2-Dichloroethane
20. Dimethyl Terephthalate
21. Ethylene Oxide
22. Formaldehyde
23. Formic Acid
24. Glyoxal
25. Hydrogen Cyanide
26. Isobutyric Acid
27. Isophthalic Acid
28. Maleic Anhydride
29. Methyl Ethyl Ketone
30. a-Methyl Styrene
31. Phenol
32. Phthalic Anhydride
33. Propionic Acid
34. Propylene Oxide (tert butyl hydroperoxide)
35. Styrene
36. Terephthalic Acid

Thirteen of the 36 chemicals contain an aromatic ring or rings. These 13 chemicals belong to each of the 11 groups listed above except the nitriles, oxides, and halogenated alkanes.

Most of these chemicals are structurally simple. The acid anhydrides, aldehydes, esters, and ketones, contain a carbonyl group. The alcohols, nitriles, oxides, and peroxides also contain reactive functional groups.[2]

The air oxidation chemicals have widely varying physical and chemical characteristics. They exist as solids, liquids, or gases at ambient condition, and most have characteristic odors.

2.2.2 Uses of Air Oxidation Chemicals

Air oxidation chemicals have many uses. They are used in production of plastics, textile fibers, rubber, surface coatings, dyes, food additives, fragrances, adhesives, drugs, and other substances.

There are two important characteristics of the air oxidation chemicals in general. First, many air oxidation chemicals serve as intermediate chemicals in the production of several other chemicals, which in turn have numerous end uses and final products. Second, while the number of uses of air oxidation chemicals is large, the major end uses are not very numerous. Plastics and textile fibers account for the bulk of production of the air oxidation chemicals studied here.[3] Table 2-2 lists the major use of each identified air oxidation chemical.[4,5]

2.2.3 Companies and Production of Air Oxidation Chemicals

Fifty-nine companies produce one or more of the 36 air oxidation chemicals. Table 2-3 gives a listing of the companies and the chemicals produced by each company.[6,7] Of the 59 companies, 43 companies produce one or two chemicals; 14 produce from three to nine chemicals; and two produce 10 or more. Celanese Corporation and Monsanto each produce the largest number, 10.

A major share of the organic chemicals partially or fully produced by air oxidation processes are controlled by large multi-line chemical companies, chemical divisions, or subsidiaries of major oil companies, or multi-industry companies with chemical process operations. Table 2-4 gives the single, largest producer for each chemical and the percent of the chemical's total capacity owned by that company.[8,9] Other major producers are listed if the largest producer does not control a major share of the chemical's total production. Thirty-nine percent, or 14 out of 36 identified air oxidation chemicals, have an annual production greater than a billion pounds per year. Table 2-5 lists the annual production capacities of the identified air oxidation chemical.[10,11] In general, the higher the production volume of the air oxidation chemical, the less percent of total capacity any one company will own. Those chemicals that are produced by only one company are typically produced in small volumes.

2.2.4 Location of Air Oxidation Plants

There are currently 161 air oxidation process facilities operating in the United States. Forty-seven of these are located in ozone national ambient air quality standards (NAAQS) non-attainment areas. Table 2-6 gives

TABLE 2-2. MAJOR END USE OF EACH IDENTIFIED SOCMI AIR OXIDATION CHEMICAL

1.	Acetaldehyde	Intermediates - Drugs - Polymers - Paints
2.	Acetic Acid	Intermediates - Polymers - Drugs - Solvents - Paints
3.	Acetone	Intermediates - Paints - Drugs - Solvent
4.	Acetonitrile	Solvent - Intermediates
5.	Acetophenone	Solvent - Drugs - Polymers - Paints
6.	Acrolein	Drugs - Intermediates
7.	Acrylic Acid	Polymers - Paints
8.	Acrylonitrile	Polymers - Drugs
9.	Anthraquinone	Paints
10.	Benzaldehyde	Intermediates - Drugs - Paints
11.	Benzoic Acid	Drugs - Polymers - Paints
12.	1,3-Butadiene	Intermediate - Polymers
13.	p-t-Butyl Benzoic Acid	Intermediate
14.	n-Butyric Acid	Polymers - Drugs
15.	Crotonic Acid	Polymers - Drugs - Intermediates
16.	Cumene Hydroperoxide	Intermediate
17.	Cyclohexanol	Intermediate - Solvent
18.	Cyclohexanone	Intermediate - Solvent
19.	1,2-Dichloroethane	Intermediate - Solvent
20.	Dimethyl Terephthalate	Polymers
21.	Ethylene Oxide	Drug - Intermediate
22.	Formaldehyde	Intermediate - Polymers - Solvent
23.	Formic Acid	Intermediate
24.	Glyoxal	Intermediate - Polymers
25.	Hydrogen Cyanide	Intermediate - Drugs
26.	Isobutyric Acid	Solvent - Drugs
27.	Isophthalic Acid	Polymers - Paints
28.	Maleic Anhydride	Polymers - Intermediate
29.	Methyl Ethyl Ketone	Solvent
30.	a-Methyl Styrene	Polymers
31.	Phenol	Polymers - Intermediate
32.	Phthalic Anhydride	Polymers - Drugs - Paints
33.	Propionic Acid	Drug
34.	Propylene Oxide	Intermediate
35.	Styrene	Polymer - Intermediate
36.	Terephthalic Acid	Polymers - Drugs - Paints

TABLE 2-3. COMPANIES PRODUCING SYNTHETIC ORGANIC CHEMICALS USING AIR OXIDATION PROCESSES

Company	Chemicals
Allied Chemical Co.	Acetone, Acetophenone, Cumene Hydroperoxide, a-Methyl Styrene, Phenol, Phthalic Anhydride
American Cyanamid Co.	Glyoxal
Amoco	Terephthalic Acid
Amoco-Standard Oil	Isophthalic Acid, Maleic Anhydride
Ashland Oil, Inc.	Maleic Anhydride
BASF Wyandotte Corp.	Phthalic Anhydride
Borden, Inc.	Formaldehyde
Celanese Corp.	Acetaldehyde, Acetic Acid, Acrylic Acid, n-Butyric Acid, Cyclohexanol, Cyclohexanone, Formaldehyde, Formic Acid, Methyl Ethyl Ketone, Propionic Acid
Chembond	Formaldehyde
Chevron Chemical Co.	Phthalic Anhydride
Ciba-Geigy Corp.	Hydrogen Cyanide
Clark Oil & Refining Corp.	Acetone, a-Methyl Styrene, Phenol
Continental Oil Co.	1,2-Dichloroethane
Co-polymer Rubber and Chemical Corp.	1,3-Butadiene
Crompton & Knowles Corp.	Benzaldehyde
Degussa Corp.	Hydrogen Cyanide
Denka Chemical Co.	Maleic Anhydride
Diamond Shamrock	1,2-Dichloroethane
Dow Badische Co.	Cyclohexanol, Cyclohexanone

TABLE 2-3 (Continued). COMPANIES PRODUCING SYNTHETIC ORGANIC CHEMICALS USING AIR OXIDATION PROCESSES

Company	Chemicals
Dow Chemical, USA	Acetone, Ethylene Oxide, Hydrogen Cyanide, Phenol, 1,2-Dichloroethane
DuPont	Acetonitrile, Acrylonitrile, Cyclohexanol, Cyclohexanone, Formaldehyde, Hydrogen Cyanide, Terephthalic Acid
Eastman Kodak Co.	Acetaldehyde, Acetic Acid, n-Butyric Acid, Crotonic Acid, Isobutyric Acid, Terephthalic Acid
El Paso Natural Gas	1,3-Butadiene
Exxon Corp.	Phthalic Anhydride
Firestone Tire & Rubber Co.	1,3 Butadiene
GAF Corp.	Formaldehyde
Georgia-Pacific Corp.	Acetone, Formaldehyde, a-Methyl Styrene, Phenol
Getty Oil Co.	Acetone, Acetophenone, a-Methyl Styrene, Phenol
B.F. Goodrich Chemical	1,2-Dichloroethane
Gulf Oil Corp.	Formaldehyde
Hercofina	Dimethyl Terephthalate, Terephthalic Acid
Hercules, Inc.	Formaldehyde, Hydrogen Cyanide
Hocker	Formaldehyde
ICI Americas Inc.	1,2-Dichloroethane
Inter'l Minerals & Chemical Corp.	Formaldehyde
Kalama Chemical, Inc.	Benzoic Acid, Phenol
Koppers Co., Inc.	Phthalic Anhydride

TABLE 2-3 (Continued). COMPANIES PRODUCING SYNTHETIC ORGANIC CHEMICALS USING AIR OXIDATION PROCESSES

Company	Chemicals
Monsanto Co.	Acetone, Acrylonitrile, Benzoic Acid, Cyclohexanol, Cyclohexanone, Formaldehyde, Hydrogen Cyanide, Maleic Anhydride, Phenol, Phthalic Anhydride
Nipro, Inc.	Cyclohexanol, Cyclohexanone
Northwest Indust., Inc.	Benzoic Acid
Olin Corp.	Propylene Oxide
Oxirane Corp.	Propylene Oxide, Styrene
Pacific RC	Formaldehyde
Pfizer, Inc.	Benzoic Acid, Maleic Anhydride, Phenol
PPG Indust., Inc.	1,2-Dichloroethane
Reichhold Chems., Inc.	Formaldehyde, Maleic Anhydride
Rohm and Haas Co.	Hydrogen Cyanide, Acrylic Acid
Shell Chemical Co.	Acetone, p-t-Butyl Benzoic Acid, Phenol, 1,2-Dichloroethane
Standard Oil Co. (OH)	Acetonitrile, Acrylonitrile, Hydrogen Cyanide
Stauffer Chemi. Co.	1,2-Dichloroethane
Stepan Chemical Co.	Phthalic Anhydride
Tenneco, Inc.	Benzoic Acid, 1,3-Butadiene, Formaldehyde, Maleic Anhydride
Toms River Chemical Corp.	Anthraquinone
UCP, Inc.	Benzaldehyde
Union Carbide Corp.	Acetone, Acetophenone, Acrolein, Acrylic Acid, Ethylene Oxide, Phenol, Propionic Acid, a-Methyl Styrene

TABLE 2-3 (Concluded). COMPANIES PRODUCING SYNTHETIC ORGANIC CHEMICALS USING AIR OXIDATION PROCESSES

U.S. Steel Corp.	Acetone, Cumene Hydroperoxide, Maleic Anhydride, a-Methyl Styrene, Phenol, Phthalic Anhydride
Vulcan Material Co.	1,2-Dichloroethane
Wright Chemical Corp.	Formaldehyde

TABLE 2-4. LARGEST PRODUCERS OF IDENTIFIED SOCMI AIR OXIDATION CHEMICALS

Chemicals	Single Largest Producer	Percent of Total Capacity	Other Major Producers
Acetaldehyde	Celanese Corp.	68	-
Acetic Acid	Celanese Corp.	74	-
Acetone	Allied Chemical Corp.	17	Union Carbide Corp. Shell Chemical Co. Monsanto Co. Dow Chemical, USA U.S. Steel Chemicals
Acetonitrile	N/A	N/A	N/A
Acetophenone	N/A	N/A	N/A
Acrolein	Union Carbide Corp.	100	-
Acrylic Acid	Rohm & Haas Co.	42	Celanese Chemical Union Carbide Corp.
Acrylonitrile	Monsanto Corp.	49	E.I. DuPont
Anthraquinone	Toms River Chemical Corp.	100	-
Benzaldehyde	N/A	N/A	N/A
Benzoic Acid	Kalama Chemical, Inc.	56	Northwest Indust., Inc.
1,3-Butadiene	Tenneco	57	El Paso Natural Gas
p-t-Butyl Benzoic Acid	Shell Chemical Co.	100	-
n-Butyric Acid	Eastman Kodak Co.	100	-
Crotonic Acid	Eastman Kodak Co.	100	-
Cumene Hydroperoxide	N/A	N/A	N/A
Cyclohexanol/ Cyclohexanone	E.I. DuPont de Nemours & Co., Inc. (E.I. DuPont)	40	Monsanto Co. -
1,2-Dichloroethane	Dow Chemical Co.	35	Shell Chemical Co., PPG Industries, Inc. Diamond Shamrock Corp.
Dimethyl Terephthalate	Hercofina	75	-
Ethylene Oxide	Union Carbide Corp.	79	-
Formaldehyde	Celanese Corp.	20	Borden, Inc. E.I. DuPont Georgia-Pacific Corp.
Formic Acid	Celanese Corp.	100	-
Glyoxal	American Cyanamid	100	-

TABLE 2-4 (Continued). LARGEST PRODUCERS OF IDENTIFIED SOCMI AIR OXIDATION CHEMICALS

Chemicals	Single Largest Producer	Percent of Total Capacity	Other Major Producers
Hydrogen Cyanide	E.I. DuPont	53	Rohm and Haas Co.
Isobutyric Acid	Eastman Kodak Co.	100	-
Isophthalic Acid	Amoco-Standard Oil Co.	100	-
Maleic Anhydride	Monsanto Co.	24	Ashland Chemical Co. U.S. Steel Chemicals Amoco-Chemicals
Methyl Ethyl Ketone	Celanese Corp.	100	-
α-Methyl Styrene	Allied Chemical Corp.	45	U.S. Steel Chemicals
Phenol	Allied Chemical Corp.	18	Monsanto Co. Shell Chemical Co. U.S. Steel Chemicals Dow Chemical, USA Union Carbide Corp.
Phthalic Anhydride	Koppers Co., Inc.	26	Monsanto Co. U.S. Steel Corp. Stepan Chemical Co.
Propionic Acid	Union Carbide Corp.	100	-
Propylene Oxide	Oxirane Corp.	100	-
Styrene	Oxirane Corp.	100	-
Terephthalic Acid	Amoco	58	E.I. DuPont

N/A = Information not available.

TABLE 2-5. ANNUAL PRODUCTION CAPACITY OF THE IDENTIFIED SOCMI AIR OXIDATION CHEMICALS

	Chemical	Capacity in Gigagrams Per Year
1.	Acetaldehyde	630
2.	Acetic Acid	770
3.	Acetone	930
4.	Acetonitrile	N/A
5.	Acetophenone	N/A
6.	Acrolein	27
7.	Acrylic Acid	428
8.	Acrylonitrile	880
9.	Anthraquinone	2[a]
10.	Benzaldehyde	N/A
11.	Benzoic Acid	145
12.	1,3-Butadiene	410
13.	p-t-Butyl Benzoic Acid	3[b,c]
14.	n-Butyric Acid	6[c,d]
15.	Crotonic Acid	6
16.	Cumene Hydroperoxide	N/A
17.	Cyclohexanol	[e]
18.	Cyclohexanone	925[e]
19.	1,2-Dichloroethane	5452
20.	Dimethyl Terephthalate	890
21.	Ethylene Oxide	1430
22.	Formaldehyde	3900
23.	Formic Acid	7
24.	Glyoxal	N/A
25.	Hydrogen Cyanide	620
26.	Isobutyric Acid	5[c,d]
27.	Isophthalic Acid	66
28.	Maleic Anhydride	200
29.	Methyl Ethyl Ketone	40
30.	a-Methyl Styrene	24
31.	Phenol	1472
32.	Phthalic Anhydride	572
33.	Propionic Acid	86
34.	Propylene Oxide	181
35.	Terephtnalic Acid	2235
36.	Styrene	635

N/A = Data not available.

[a] Letter from Bobsein, W.P., Toms River Chem. Corp., to Evans, L.B., EPA, February 11, 1980.

[b] Estimated based on data given in letter from Haxby, L.P., Shell Oil Co., to Evans, L.B., EPA, January 9, 1980.

[c] Memo from Galloway, J., EEA, to SOCMI Air Oxidation File. Estimation of capacities for p-t-Butylbenzoic Acid, n-Butyric Acid, and Isobutyric Acid from company data, April 9, 1981.

[d] Estimated based on data given in letter and attachment from Edwards, J.C., Eastman Kodak Co., to Evans, L.B., EPA, February 6, 1980.

[e] Production capacity of cyclohexanol and cyclohexanone have been reported together.

TABLE 2-6. AIR OXIDATION PROCESS FACILITIES

Nonattainment Area	Primary Air-Oxidation Product(s) (Manufacturing Process In Parentheses)	Company	Location	Capacity (Gg/yr) (Including All By-Products)
	Acetaldehyde	Celanese Chemical	Bay City, Texas	136
	Acetaldehyde	Celanese Chemical	Clear Lake, Texas	295
	Acetaldehyde	Texas Eastman	Longview, Texas	200
	Acetic Acid (Wacker)	Celanese Chemical	Bay City, Texas	90
	Acetic Acid (Wacker)	Celanese Chemical	Clear Lake, Texas	227
	Acetic Acid/Formic Acid/MEK/Butyric Acid/Propionic Acid	Celanese Chemical	Pampa, Texas	298
	Acetic Acid (Wacker)	Tennessee Eastman	Kingsport, Tennessee	204
Yes	Acetone/Phenol	Allied Chemical	Frankford, Pennsylvania	446
Yes	Acetone/Phenol	Clark Chemical	Blue Island, Illinois	66
	Acetone/Phenol	Dow Chemical	Oyster Creek, Texas	338
	Acetone/Phenol	Georgia Pacific	Plaquemine, Louisiana	240
	Acetone/Phenol	Getty Refining	El Dorado, Kansas	70
Yes	Acetone/Phenol	Monsanto Chemical	Chocolate Bayou, Texas	363
Yes	Acetone/Phenol	Shell Chemical	Deer Park, Texas	363
Yes	Acetone/Phenol	Amoco-Std. Oil	Richmond, California	40
	Acetone/Phenol	Union Carbide	Bound Brook, New Jersey	113
	Acetone/Phenol	Union Carbide	Penuelas, Puerto Rico	162
	Acetone/Phenol	U.S. Steel Chemical	Haverhill, Ohio	380
	Acrylic Acid	Celanese Chemical	Clear Lake, Texas	104
	Acrylic Acid	Celanese Chemical	Pampa, Texas	34
Yes	Acrylic Acid	Rohm and Haas	Deer Park, Texas	181
	Acrylic Acid/Acrolein	Union Carbide	Taft, Louisiana	136
	Acrylonitrile	DuPont	Memphis, Tennessee	140
	Acrylonitrile	DuPont	Beaumont, Texas	181
	Acrylonitrile	Monsanto Chemical	Alvin, Texas	240
	Acrylonitrile	Monsanto Chemical	Texas City, Texas	256
	Acrylonitrile	Vistron (SOHIO)	Lima, Ohio	200
Yes	Anthraquinone	Toms River Chemical	Toms River, New Jersey	1.8[a]

TABLE 2-6 (Continued). AIR OXIDATION PROCESS FACILITIES

Nonattainment Area	Primary Air-Oxidation Product(s) (Manufacturing Process In Parentheses)	Company	Location	Capacity (Gg/yr) (Including All By-Products)
Yes	Benzaldehyde	Crompton and Knowles	Fair Lawn, New Jersey	Not Reported
	Benzoic Acid/Phenol	Kalama Chemical	Kalama, Washington	81
	Benzoic Acid/Phenol	Northwest Indust.	Beaumont, Texas	18
	Benzoic Acid/Phenol	Northwest Indust.	Chattanooga, Tennessee	23
	Benzoic Acid/Phenol	Pfizer Chemicals	Terre Haute, Indiana	15
Yes	Benzoic Acid/Phenol	Tenneco Chemicals	Garfield, New Jersey	7
Yes	Benzoic Acid/Phenol	Monsanto Chemical	St. Louis, Missouri	1
	1,3-Butadiene	Firestone	Orange, Texas	54
Yes	1,3-Butadiene	Tenneco	Houston, Texas	236
	1,3-Butadiene	Copolymer Rubber	Baton Rouge, Louisiana	27
	1,3-Butadiene	El Paso Natural Gas	Odessa, Texas	93
	p-t-Butylbenzoic Acid	Shell Chemical	Martinex, California	Not Reported, Estimated To Be 3.[b,c]
	n-Butyric Acid	Tennessee Eastman	Kingsport, Tennessee	Not Reported, Estimated To Be 6.[c,d]
	Crotonic Acid	Tennessee Eastman	Kingsport, Tennessee	6
	Cyclohexanone/Cyclohexanol	Badische	Freeport, Texas	140
	Cyclohexanone/Cyclohexanol	Celanese Chemical	Bay City, Texas	45
	Cyclohexanone/Cyclohexanol	DuPont	Orange, Texas	142
	Cyclohexanone/Cyclohexanol	DuPont	Victoria, Texas	231
	Cyclohexanone/Cyclohexanol	Monsanto Chemical	Pensacola, Florida	227
	Cyclohexanone/Cyclohexanol	Nipro	Augusta, Georgia	139

TABLE 2-6 (Continued). AIR OXIDATION PROCESS FACILITIES

Nonattainment Area	Primary Air-Oxidation Product(s) (Manufacturing Process In Parentheses)	Company	Location	Capacity (Gg/yr) (Including All By-Products)
Yes	Terephthalic Acid (TPA)	DuPont	Old Hickory, Tennessee	213
	Terephthalic Acid (TPA)	DuPont	Wilmington, North Carolina	485
	Dimethyl Terephthalate (DMT)	Carolina Eastman	Columbia, South Carolina	227
	TPA	Tennessee Eastman	Kingsport, Tennessee	227
	DMT/TPA	Hercofina	Wilmington, North Carolina	703
	DMT	Hercofina	Spartanburg, South Carolina	75
	TPA	Amoco	Charleston, South Carolina	454
	TPA	Amoco	Decatur, Alabama	743
	Ethylene Oxide	Dow Chemical	Freeport, Texas	91
	Ethylene Oxide	Dow Chemical	Plaquemine, Louisiana	204
	Ethylene Oxide	Union Carbide	Seadrift, Texas	385
	Ethylene Oxide	Union Carbide	Taft, Louisiana	500
	Ethylene Oxide	Union Carbide Caribe	Ponce, Puerto Rico	250
	Formaldehyde (Silver)	Borden, Inc.	Demopolis, Alabama	45
	Formaldehyde (Silver)	Borden, Inc.	Diboll, Texas	36
	Formaldehyde (Silver)	Borden, Inc.	Fayetteville, North Carolina	107
Yes	Formaldehyde (Silver)	Borden, Inc.	Louisville, Kentucky	36
	Formaldehyde (Silver)	Borden, Inc.	Sheboygan, Wisconsin	59
Yes	Formaldehyde (Silver)	Borden, Inc.	Fremont, California	102
Yes	Formaldehyde (Silver)	Borden, Inc.	Kent, Washington	36
	Formaldehyde (Silver)	Borden, Inc.	La Grande, Oregon	30
	Formaldehyde (Silver)	Borden, Inc.	Missoula, Montana	40
	Formaldehyde (Silver)	Borden, Inc.	Springfield, Oregon	30
	Formaldehyde (Silver)	Borden, Inc.	Geismar, Louisiana	13
Yes	Formaldehyde (Mixed Metal)	Celanese Chemical	Newark, New Jersey	53
	Formaldehyde (Mixed Metal)	Celanese Chemical	Rock Hill, South Carolina	53
	Formaldehyde (Silver)	Celanese Chemical	Bishop, Texas	80
Yes	Formaldehyde (Silver)	E.I. DuPont Denemours	Belle, West Virginia	227
	Formaldehyde (Silver)	E.I. DuPont Denemours	Healing Springs, NC	100
Yes	Formaldehyde (Silver)	E.I. DuPont Denemours	LaPorte, Texas	145
Yes	Formaldehyde (Silver)	E.I. DuPont Denemours	Linden, New Jersey	73
	Formaldehyde (Silver)	E.I. DuPont Denemours	Toledo, Ohio	122

TABLE 2-6 (Continued). AIR OXIDATION PROCESS FACILITIES

Nonattainment Area	Primary Air-Oxidation Product(s) (Manufacturing Process In Parentheses)	Company	Location	Capacity (Gg/vr) (Including All By-Products)
	Formaldehyde (Mixed Metal)	GAF Corporation	Calvert City, Kentucky	45
	Formaldehyde (Mixed Metal)	Georgia-Pacific	Albany, Oregon	45
	Formaldehyde (Mixed Metal)	Georgia-Pacific	Columbus, Ohio	77
	Formaldehyde (Mixed Metal)	Georgia-Pacific	Coos Bay, Oregon	35
	Formaldehyde (Silver)	Georgia-Pacific	Crossett, Arkansas	27
	Formaldehyde (Silver)	Georgia-Pacific	Crossett, Arkansas	45
	Formaldehyde (Mixed Metal)	Georgia-Pacific	Lufkin, Texas	45
	Formaldehyde (Mixed Metal)	Georgia-Pacific	Russelville, South Carolina	90
	Formaldehyde (Mixed Metal)	Georgia-Pacific	Taylorsville, Mississippi	55
	Formaldehyde (Silver)	Georgia-Pacific	Vienna, Georgia	45
	Formaldehyde (Mixed Metal)	Chembond	Andalusia, Alabama	32
	Formaldehyde (Mixed Metal)	Chembond	Springfield, Oregon	32
	Formaldehyde (Silver)	Chembond	Springfield, Oregon	32
	Formaldehyde (Mixed Metal)	Chembond	Winnfield, Alabama	32
	Formaldehyde (Mixed Metal)	Gulf Oil	Vicksburg, Mississippi	23
	Formaldehyde (Silver)	Hercules	Louisiana, Missouri	77
Yes	Formaldehyde (Mixed Metal)	International Minerals & Chemical	Seiple, Pennsylvania	120
Yes	Formaldehyde (Silver)	International Minerals & Chemical	Seiple, Pennsylvania	30
Yes	Formaldehyde (Silver)	Monsanto Chemical	Addyston, Ohio	55
	Formaldehyde (Silver)	Monsanto Chemical	Chocolate Bayou, Texas	88
	Formaldehyde (Silver)	Monsanto Chemical	Eugene, Oregon	45
Yes	Formaldehyde (Silver)	Monsanto Chemical	Springfield, Massachusetts	134
	Formaldehyde (Silver)	Hooker	North Tonawanda, New York	61
	Formaldehyde (Silver)	Reichhold Chemicals	Hampton, South Carolina	23
Yes	Formaldehyde (Mixed Metal)	Reichhold Chemicals	Houston, Texas	45
	Formaldehyde (Silver)	Reichhold Chemicals	Kansas City, Kansas	18
	Formaldehyde (Mixed Metal)	Reichhold Chemicals	Malvern, Arkansas	50
	Formaldehyde (Mixed Metal)	Reichhold Chemicals	Moncure, North Carolina	45
Yes	Formaldehyde (Mixed Metal)	Reichhold Chemicals	Tacoma, Washington	23
	Formaldehyde (Silver)	Reichhold Chemicals	Tuscaloosa, Alabama	34
	Formaldehyde (Mixed Metal)	Reichhold Chemicals	White City, Oregon	102
Yes	Formaldehyde (Mixed Metal)	Tenneco	Fords, New Jersey	57

TABLE 2-6 (Continued). AIR OXIDATION PROCESS FACILITIES

Nonattainment Area	Primary Air-Oxidation Product(s) (Manufacturing Process In Parentheses)	Company	Location	Capacity (Gg/yr) (Including All By-Products)
Yes	Formaldehyde (Silver)	Tenneco	Fords, New Jersey	27
Yes	Formaldehyde (Silver)	Tenneco	Garfield, New Jersey	45
	Formaldehyde (Silver)	Pacific RC	Eugene, Oregon	43
	Formaldehyde (Mixed Metal)	Wright Chemical	Riegelwood, North Carolina	36
	Glyoxal	American Cyanamid	Charlotte, North Carolina	Not Reported
	Hydrogen Cyanide	Ciba-Geigy	St. Gabriel, Louisiana	40
	Hydrogen Cyanide	Degussa	Theodore, Alabama	24
	Hydrogen Cyanide	Dow Chemical	Freeport, Texas	9
	Hydrogen Cyanide	DuPont	Memphis, Tennessee	66
	Hydrogen Cyanide	DuPont	Orange, Texas	95
	Hydrogen Cyanide	DuPont	Victoria, Texas	95
	Hydrogen Cyanide	Ciba-Geigy	Glen Falls, New York	1
	Hydrogen Cyanide	Monsanto	Texas City, Texas	63
Yes	Hydrogen Cyanide	Rohm and Haas	Deer Park, Texas	90
	Isobutyric Acid	Tennessee Eastman	Kingsport, Tennessee	Not Reported, Estimated To Be 5.[c,d]
Yes	Isophthalic Acid	Amoco-Standard Oil	Joliet, Illinois	65
	Maleic Anhydride (Benzene)	Ashland	Neal, West Virginia	27
Yes	Maleic Anhydride (Benzene)	Denka	Houston, Texas	23
Yes	Maleic Anhydride (Benzene)	Monsanto Chemical	St. Louis, Missouri	38
Yes	Maleic Anhydride (Butane)	Monsanto Chemical	St. Louis, Missouri	10
	Maleic Anhydride (Benzene)	Reichhold	Morris, Illinois	20
Yes	Maleic Anhydride (Butane)	Amoco-Standard Oil	Joliet, Illinois	27
Yes	Maleic Anhydride (Benzene)	Tenneco	Fords, New Jersey	10
Yes	Maleic Anhydride (Benzene)	U.S. Steel Chemicals	Neville Island, Pennsylvania	36
	Maleic Anhydride (Benzene)	Pfizer	Terre Haute, Indiana	9

TABLE 2-6 (Concluded). AIR OXIDATION PROCESS FACILITIES

Nonattainment Area	Primary Air-Oxidation Product(s) (Manufacturing Process In Parentheses)	Company	Location	Capacity (Gg/_r) (Including All By-Products)
Yes	Phathalic Anhydride (Xylene)	Allied Chemical	El Segundo, California	16
Yes	Phathalic Anhydride (Xylene)	Basf Wyandotte	Kearny, New Jersey	68
	Phathalic Anhydride (Xylene)	Exxon	Baton Rouge, Louisiana	60
Yes	Phathalic Anhydride (Naphthalene)	Koppers	Bridgeville, Pennsylvania	40
Yes	Phathalic Anhydride (Xylene)	Koppers	Cicero, Illinois	107
Yes	Phathalic Anhydride (Naphthalene)	Monsanto Chemical	Bridgeport, New Jersey	40
	Phathalic Anhydride (Xylene)	Monsanto Chemical	Texas City, Texas	60
Yes	Phathalic Anhydride (Xylene)	Chevron	Richmond, California	23
	Phathalic Anhydride (Xylene)	Stepan	Millsdale, Illinois	76
Yes	Phathalic Anhydride (Naphthalene)	U.S. Steel	Neville Island, Pennsylvania	82
	Propionic Acid	Union Carbide	Texas City, Texas	86
Yes	Propylene Oxide/Styrene	Oxirane	Channelview, Texas	816
	1,2-Dichloroethane	Conoco Chemicals	Lake Charles, Louisiana	266
Yes	1,2-Dichloroethane	Diamond Shamrock	Deer Park, Texas	145
Yes	1,2-Dichloroethane	Diamond Shamrock	La Porte, Texas	454
	1,2-Dichloroethane	Dow Chemical	Freeport, Texas	726
	1,2-Dichloroethane	Dow Chemical	Oyster Creek, Texas	500
	1,2Dichloroethane	Dow Chemical	Plaquemine, Louisiana	816
	1,2-Dichloroethane	Ethyl	Baton Rouge, Louisiana	318
Yes	1,2-Dichloroethane	Ethyl	Pasadena, Texas	118
	1,2-Dichloroethane	B.F. Goodrich Chemical	Calvert City, Kentucky	454
	1,2-Dichloroethane	ICI Americas Petrochemicals	Baton Rouge, Louisiana	234
	1,2-Dichloroethane	P.P.G. Industries Chemicals-US	Lake Charles, Louisiana	703
Yes	1,2-Dichloroethane	Shell Chemical	Deer Park, Texas	635
	1,2-Dichloroethane	Shell Chemical	Norco, Louisiana	318
Yes	1,2-Dichloroethane	Stauffer Chemical	Long Beach, California	45
	1,2-Dichloroethane	Vulcan Chemicals	Geismar, Louisiana	159

[a] Op. cit., see Reference a for Table 2-5.

[b] Op. cit., see Reference b for Table 2-5.

[c] Op. cit., see Reference c for Table 2-5.

[d] Op. cit., see Reference d for Table 2-5.

a listing of the air oxidation manufacturing processes and the facilities employing each process.[12,13] The plant location, capacity, and major product(s) are given for each facility. Those facilities located in nonattainment areas are so indicated.

Although air oxidation industries are scattered throughout several states, many are located near refineries, which are located near domestic sources of oil or points of entry for imported oil. Some of the petrochemical plants border refineries, thus permitting an easy exchange of products. This results in a heavy concentration of chemical production along the Gulf Coast (Texas and Louisiana) and the East Coast, particularly in New Jersey and Pennsylvania.

Air oxidation plants are located in 27 states; over half of the 161 plants are located in the Gulf Coast and the East Coast. Twenty-eight of the 36 air oxidation chemicals are produced in Texas. Louisiana and New Jersey each produce 33 percent or more of the 36 air oxidation chemicals.

2.3 AIR OXIDATION PRODUCTION PROCESSES

The only determinant for classification as an air oxidation chemical is the process by which the chemical is produced. Some chemicals identified as air oxidation chemicals in Section 2.2.1 can be made by non-air oxidation processes.[14-16] Table 2-7 shows the percentages of air oxidation production of each of the chemicals.[17]

Despite the large variation in reaction types used to produce air oxidation chemicals, air oxidation processes can be grouped together because they have one very important characteristic in common, the need to vent large quantities of inert material containing VOC to the atmosphere. These inerts, predominantly nitrogen, are present because air contains 20.9 percent oxygen and 78.1 percent nitrogen by volume on a dry basis. The nitrogen in the air passes through the reaction unreacted. The exact quantity of nitrogen and unreacted oxygen emitted is a function of the amount of excess air used in the production process. The following sections present a discussion of the reaction types used for the production of air oxidation chemicals and the important factors which determine the amount of excess air used.

2.3.1 Reaction Types

The principal types of oxidation reactions that take place in the production of air oxidation chemicals are:

1. Dehydrogenation,
2. Introduction of an oxygen atom,
3. Destruction of carbon-carbon bonds,
4. Use of oxygen carrier,
5. Peroxidation,
6. Ammoxidation,
7. Oxidative condensation, and
8. Oxyhalogenation.

Dehydrogenation is illustrated in the transformation of a primary alcohol to an aldehyde:

TABLE 2-7. PERCENTAGE PRODUCTION OF SOCMI CHEMICALS BY AIR OXIDATION

Product	% of Product Manufactured by Air Oxidation
1. Acetaldehyde	99.7
2. Acetic Acid	40
3. Acetone	65
4. Acetonitrile	No Data
5. Acetophenone	No Data
6. Acrolein	52
7. Acrylic Acid	94
8. Acrylonitrile	100
9. Anthraquinone	No Data
10. Benzaldehyde	No Data
11. Benzoic Acid	100
12. 1,3-Butadiene	23
13. p-t-Butyl Benzoic Acid	No Data
14. n-Butyric Acid	No Data
15. Crotonic Acid	No Data
16. Cumene Hydroperoxide	No Data
17. Cyclohexanol	81
18. Cyclohexanone	81
19. 1,2-Dichloroethane	96
20. Dimethyl Terephthalate	100
21. Ethylene Oxide	51
22. Formaldehyde	100
23. Formic Acid	23
24. Glyoxal	No Data
25. Hydrogen Cyanide	100
26. Isobutyric Acid	No Data
27. Isophthalic Acid	100
28. Maleic Anhydride	80
29. Methyl Ethyl Ketone	11[a]
30. a-Methyl Styrene	100[a]
31. Phenol	98
32. Phthalic Anhydride	100
33. Propionic Acid	62[a]
34. Propylene Oxide	20
35. Styrene	18
36. Terephthalic Acid	100

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*Produced by air or oxygen oxidation.

[a] SRI International 1978 Directory of Chemical Producers, United States of America.

$$C_2H_5OH + \frac{1}{2}O_2 = CH_3CHO + H_2O$$

or of a secondary alcohol to a ketone:

$$CH_3CHOHCH_3 + \frac{1}{2}O_2 = CH_3COCH_3 + H_2O$$

or of an alkane to alkene:

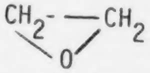
$$CH_3CH_2CH_2CH_3 + O_2 = CH_2CHCHCH_2 + 2H_2O$$

An atom of oxygen may be introduced into a molecule, as is illustrated by the oxidation of an aldehyde to an acid:

$$CH_3CHO + \frac{1}{2}O_2 = CH_3COOH$$

or of a hydrocarbon to an oxide:

$$CH_2CH_2 + \frac{1}{2}O_2 =$$



A combination of the above may occur, as in the preparation of aldehydes from hydrocarbons:

$$CH_4 + O_2 = CH_2O + H_2O$$

or of benzoic acid from toluene:

$$C_6H_5CH_3 + 1\frac{1}{2}O_2 = C_6H_5COOH + H_2O$$

A combination of dehydrogenation, oxygen introduction, and destruction of carbon-carbon bond may all occur in the same process of oxidation, e.g., in the oxidation of naphthalene to phthalic anhydride:

$$C_{10}H_8 + 4\frac{1}{2}O_2 = C_8H_4O_3 + 2H_2O + 2CO_2$$

Oxidation may be accomplished indirectly through the use of intermediate or oxygen carrier:

$$C_2H_4 + 2CuCl_2 + H_2O \xrightarrow{PdCl_2} CH_3CHO + HCl + 2CuCl$$

Peroxidation occurs readily under certain conditions. Thus, some reactions occur directly with air when catalyzed by heavy metal salts:

Cumene + air = Cumene Hydroperoxide

Ammoxidation is a process for the formation of nitriles by the action of ammonia in the presence of air or oxygen on olefins, organic acids, or other alkyl group of alkylated aromatics:

$$C_3H_6 + NH_3 + 1\frac{1}{2}O_2 = CH_2CHCN + 3H_2O$$

Oxidative condensation occurs when two molecules combine with each other with the introduction of oxygen atoms and removal of small molecules like water:

$$2CH_3CHO + O_2 = CH_3COOOCCH_3 + H_2O$$

Oxyhalogenation is a process in which oxygen and a halogen reacts with an organic compound:

$$C_2H_4 + \frac{1}{2}O_2 + 2HCl = ClCH_2CH_2Cl + H_2O$$

In some reactions, several types of oxidation take place at the same time resulting in co-products and by-products. A co-product is formed simultaneously along with the desired reaction product and is primarily marketable. A common example of such a reaction would be air oxidation of cyclohexane, where cyclohexanol and cyclohexanone are produced as co-products.[18] By-products, on the other hand, result from competitive side or parallel reactions occurring along with the main reaction. It is generally a "leftover" of the process, which in some cases is marketable. For example, in the manufacture of acrylonitrile by ammoxidation of propylene, acetonitrile and hydrogen cyanide are produced as by-products.[19] Also, in some cases, the product of the air oxidation reaction is not the end product of the production process, such as the production of ethylbenzene hydroperoxide which is used to make styrene. Table 2-8 lists co-products and by-products for those air oxidation processes with more than one product.

2.3.2 Raw Materials

The principal raw materials for the manufacture of air oxidation chemicals are olefins (ethylene and propylene), C_4 fractions (butanes and butenes) and aromatics. Table 2-9 shows the air oxidation chemicals divided into these categories. Because of the vast number of different synthesis routes available, several of the air oxidation chemicals fall into more than one classification.

In air oxidation processes, there is a large contribution of feedstock to overall price of the chemical, and thus, there exists a strong incentive to find cheaper (or less refined) or more readily available feedstocks. This can be seen in the gradual switch to butane feedstock in the manufacture of maleic anhydride. Originally, maleic anhydride was produced via air oxidation of benzene. With the increase in benzene costs, all but one maleic anhydride plant has switched to n-butane feeds. It is expected that the one remaining benzene-based product will be converted to the butane-based process in the near future.[20,30]

Butanes can be obtained from natural gas, from crude oil, or as a by-product of olefins production. Aromatics can be obtained from oil as a product of catalytic reforming or from coal as a by-product of coking. At present, the largest source is from catalytic cracking during oil refining; however, this may change in the future as more synthetic fuel plants based on coal are built. Several of the air oxidation chemicals are made from

TABLE 2-8. AIR OXIDATION PROCESSES WITH CO-PRODUCT(S) AND BY-PRODUCT(S)

Process	Co-Products	By-Products
Butane Oxidation II	Acetic Acid, Methyl Ethyl Ketone	Formic Acid, n-Butyric Acid, Propionic Acid
Cyclohexane Oxidation	Cyclohexanol, Cyclohexane	
Ethylbenzene Hydroperoxidation	Styrene, Propylene Oxide	
Cumene Hydroperoxidation	Acetone, Phenol	Cumene Hydroperoxide, Acetophenone, α-Methyl Styrene
Toluene Oxidation	Phenol, Benzoic Acid	
p-Xylene Oxidation	Dimethyl Terephthalate, Terephthalic Acid	
Propylene Oxidation	Acrylic Acid	Acrolein
Propylene Ammoxidation	Acrylonitrile, Hydrogen Cyanide	Acetonitrile

TABLE 2-9. BASIC RAW MATERIALS FOR AIR OXIDATION CHEMICALS

Ethylene Based	Propylene Based	Butane Based	Aromatic Based	Other
Acetaldehyde	Acrolein	Acetic Acid	Acetone	Formaldehyde (Methanol from Syngas)
Acetic Acid	Acrylic Acid	1,3-Butadiene	Acetophenone	Hydrogen Cyanide (Methane + Ammonia)
Ethylene Oxide		n-Butyric Acid	Benzaldehyde	Hydrogen Cyanide (Ammonia + Propylene)
Glyoxal		Formic Acid	Benzoic Acid	Acetonitrile (Ammonia + Propylene)
Crotonic Acid		Isobutyric Acid	para-tert-Butyl Benzoic Acid	Acrylonitrile (Ammonia + Propylene)
		Maleic Anhydride	Cumene Hydroperoxide	
		Methyl Ethyl Ketone	Cyclohexanol	
		Propionic Acid	Cyclohexanone	
			Dimethyl Terephthalate	
			Isophthalic Acid	
			Methyl Styrene	
			Phenol	
			Phthalic Anhydride	
			Styrene	
			Terephthalic Acid	

natural gas-based petrochemicals. Alternative routes to these chemicals utilizing oil-based feeds are being developed.

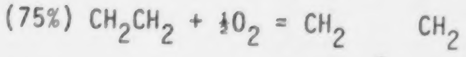
2.3.3 Reaction Characteristics

In spite of numerous reaction mechanisms, all air oxidation processes vent large quantities of inert material containing predominantly nitrogen from air and some VOC. Therefore, to quantify VOC emissions, and to select the applicable control method, it is necessary to quantify offgas flow and VOC concentrations. As discussed in Chapter 3, flow and VOC concentrations are the major process parameters which determine the economics of controlling VOC emissions by thermal or catalytic incineration. This section discusses the reaction characteristics which affect the offgas flow from air oxidation processes. Section 2.4 presents the results of the statistical analysis from which the national VOC emission profile was developed.

There are several reaction characteristics which determine the amount of offgas vented to the atmosphere. They are as follows:

1. Reaction stoichiometry,
2. Reaction phase, and
3. Explosion hazard.

2.3.3.1 Reaction Stoichiometry. In air oxidation reactions, oxygen from the air reacts with an organic reactant to produce the following: (1) product air oxidation chemical, (2) some carbon dioxide and carbon monoxide due to partial combustion of the feedstock, and (3) co-products and by-products. The total oxygen required is dependent on the extent of each reaction. The stoichiometry of the reaction and the catalyst selectivity of a process determine the theoretical amount of oxygen required for a given process. Catalyst selectivity is defined as the quotient of the amount of reaction product to the amount of converted feedstock.[21] For example, in the ethylene oxide process, ethylene reacts with oxygen to produce ethylene oxide (main reaction) and carbon dioxide according to the following equations:



$$(75\%)\ CH_2CH_2 + \tfrac{1}{2}O_2 = \underset{O}{CH_2\quad CH_2}$$

$$(25\%)\ CH_2CH_2 + 3O_2 = 2CO_2 + 2H_2O$$

$$(100\%)\ CH_2CH_2 + \frac{9}{8}\,O_2 = \frac{3}{4}\,C_2H_4O + CO_2 + H_2O$$

The molecular oxygen ratio (MOR), defined as moles of oxygen per mole of product, is 0.5 for the main reaction. However, considering the oxygen required for the combustion reaction at an average catalyst selectivity of 75 percent[22], the MOR of the overall reaction becomes 1.5.

Generally, all air oxidation processes require greater than stoichiometric amount of air to realize optimum conversion, favorable reaction rates, and to prevent explosion hazard.

2.3.3.2 Reaction Phase. Generally, air oxidation reaction can be carried out in either liquid or gas phase. Table 2-10 shows the division of

TABLE 2-10. PHASE OF THE AIR OXIDATION REACTION STEP IN THE PRODUCTION OF AIR OXIDATION CHEMICALS

	Liquid Phase		Vapor Phase
1.	Acetaldehyde	1.	Acetaldehyde
2.	Acetic Acid	2.	Acetonitrile
3.	Acetone	3.	Acrolein
5.	Acetophenone	4.	Acrylic Acid
6.	Benzaldehyde	5.	Acrylonitrile
7.	Benzoic Acid	6.	Anthraquinone
8.	p-t-Butyl Benzoic Acid	7.	1,3-Butadiene
9.	n-Butyric Acid	8.	1,2-Dichloroethane
10.	Cumene Hydroperoxide	9.	Ethylene Oxide
11.	Cyclohexanol	10.	Formaldehyde
12.	Cyclohexanone	11.	Glyoxal
13.	Dimethyl Terephthalate	12.	Hydrogen Cyanide
14.	Formic Acid	13.	Maleic Anhydride
15.	Isobutyric Acid	14.	Phthalic Anhydride
16.	Isophthalic Acid		
17.	Methyl Ethyl Ketone		
18.	a-Methyl Styrene		
19.	Phenol		
20.	Propionic Acid		
21.	Propylene Oxide (tert butyl hydroperoxide)[a]		
22.	Styrene[a]		
23.	Terephthalic Acid		

---

[a] The air oxidation step in styrene/propylene oxide manufacture is the liquid phase hydroperoxidation of ethylbenzene.

the various air oxidation processes between liquid and vapor phase. The processes are categorized according to the phase of the air oxidation reaction step, and not according to the phase of the step(s) in which the final product(s) is/are formed.

Liquid phase reactions generally utilize high molecular weight thermally unstable reactants. The reaction temperatures are low or moderate and usually require high pressures for optimum reaction rates.[23] The extent of oxidation is controlled by limiting the duration of operation, controlling the temperature and using low excess air. Large amounts of excess air may cause branching of radical precursors with formation of a multiplicity of radicals and, consequently, runaway reactions which could ultimately result in explosion.

The catalyst used in liquid phase processes may be either dissolved or suspended in finely divided form to ensure contact with the bubbles of gas-containing oxygen which pass through the liquid undergoing oxidation. To speed up the production, means must be provided for initially raising the temperature and for later removing reaction heat. Heat may be removed and temperature controlled by circulation of either the liquid being oxidized or a special cooling fluid through the reaction zone and then through an external heat exchanger. Where low temperatures and slow reaction rates are indicated, natural processes of heat flow to the atmosphere may suffice for temperature control.

In addition, liquid phase processes require adequate mixing and contact of the two immiscible phases of gaseous oxidizing agent and the liquid being oxidized. Mixing may be obtained by the use of special distributor inlets for the air, designed to spread the air throughout the liquid. Mechanical stirring or frothing of the liquid are the other methods of providing thorough mixing.

Figure 2-1 represents a schematic flowsheet of a liquid phase air oxidation process. Liquid feedstock and catalyst are fed into a reactor. The reaction is carried out by passing air through this liquid mixture at a controlled temperature and pressure. After completion of the reaction, two streams come out of the reactor, liquid and gaseous. The liquid stream usually contains the desired product, which is taken to a product recovery system consisting of a series of different unit operations (e.g., distillation, crystallization, evaporation, etc). The gaseous stream containing nitrogen, unreacted oxygen, CO_2, and some VOC is condensed or cooled and then fed into the gas separator to recover the condensable compounds before venting it to the atmosphere.

In contrast to liquid phase reactions, vapor phase air oxidation reactions can be effectively applied only to readily volatile substances that are of sufficient thermal stability to resist dissociation at elevated temperatures. The desired product must also be thermally stable to continued oxidation and must be readily separable from gaseous product. These various restrictions limit the material capable for economic processing by vapor phase air oxidation to the simpler aliphatic and aromatic series of compounds.[24]

In vapor phase air oxidation processes, a solid or vapor phase catalyst may be employed. The temperatures are usually high. Control is affected by

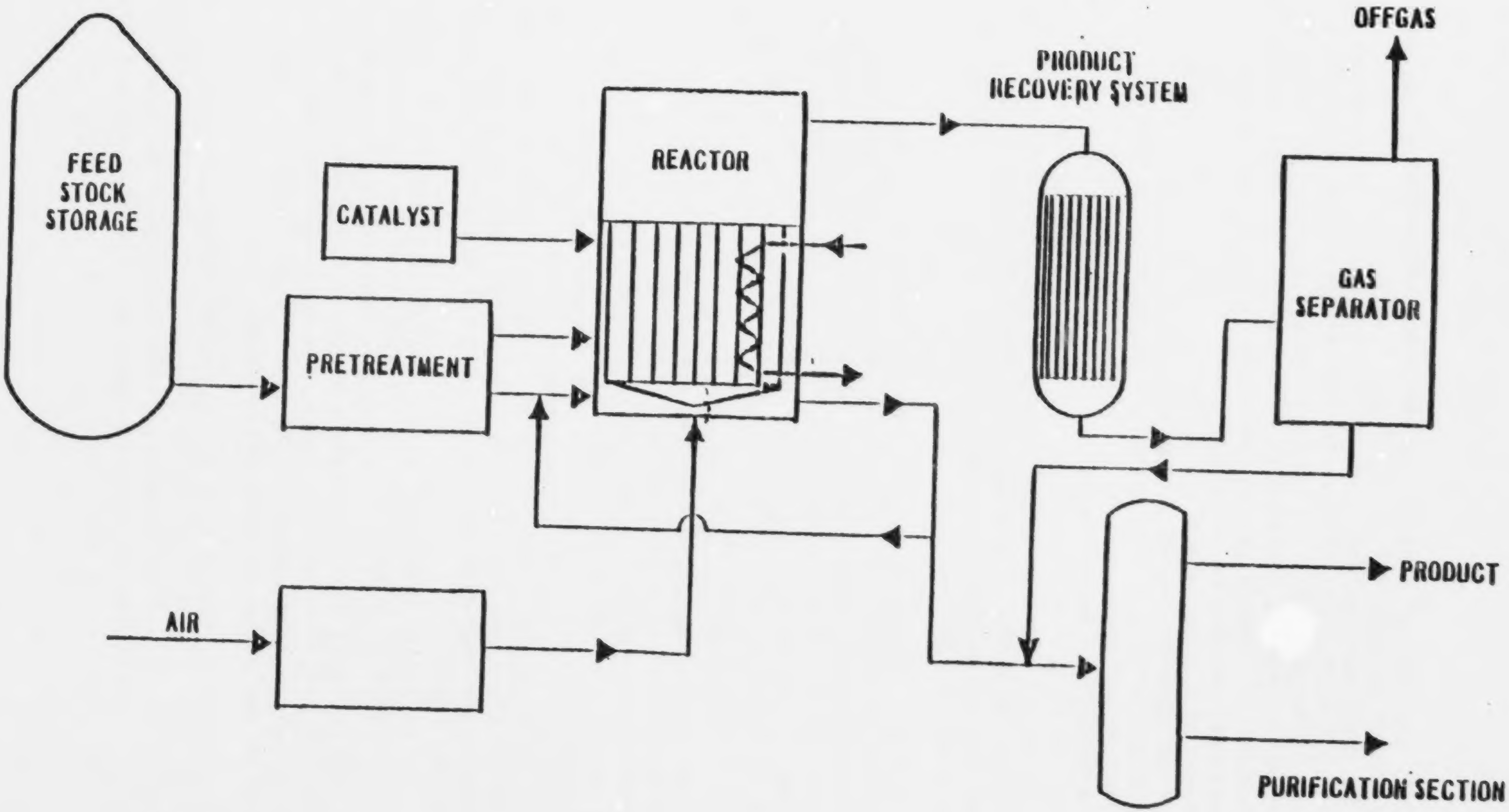

OFFGAS
PRODUCT RECOVERY SYSTEM
FEED STOCK STORAGE
CATALYST
REACTOR
GAS SEPARATOR
PRETREATMENT
AIR
PRODUCT
PURIFICATION SECTION

Figure 2-1. Schematic of a flowsheet for a liquid phase air oxidation process.

limiting the time of contact, temperature, proportion of oxygen, type of catalyst, or by combinations of these factors.

By their very nature, the vapor phase oxidation processes result in the concentration of reaction heat in the catalyst zone, from which it must be removed in large quantities at high temperature levels. Removal of heat is essential to prevent destruction of apparatus, catalyst, or raw material. Maintenance of temperature at the proper level is necessary to ensure the correct rate and degree of oxidation.[25] Figure 2-2 represents a schematic flowsheet of a vapor phase air oxidation process. The feedstock which is either in vapor or liquid phase is first vaporized, if required, and then mixed with air in a mixing chamber. The mixture is then fed at the required temperature and pressure into a reaction chamber where it comes in contact with a catalyst. After completion of the reaction, the mixture of gases coming out of the reactor is passed through a product recovery system consisting of different unit operations, which can include condensers, scrubbers, or both. The exhaust gas coming from the product recovery system containing predominantly nitrogen and some VOC, is vented to the atmosphere or to a control device.

2.3.3.3 Explosion Hazard. Many organic reactants used in air oxidation processes are inflammable and require adequate means to prevent explosion hazard. When vapors of an inflammable organic compound are mixed with air in the proper proportion, ignition can produce an explosion. An increase in temperature of a mixture of organic vapors with air expands the range of organics concentration capable of leading to an explosion. Because of the explosion hazard, many insurance regulations limit the inflammable organics concentration to 25 percent of the lower explosive limit in air. In some cases to maintain reaction conditions below the explosive limit, large quantities of excess air are used. Alternatively, low inlet concentrations can be achieved by recycling a portion of the reactor offgas back to the reactor system. Some processes, however, can operate above the explosive limit. For example, in the manufacture of formaldehyde by silver catalyst process, methanol concentration in the gas stream is maintained above the explosive limit.[26] It is, however, possible that some processes, by use of fluidized bed reactors, gas stream recycle, or utilizing sophisticated heat transfer systems may operate within the apparent explosive range.[27]

The explosion hazard of an air oxidation process is also dependent on the auto-ignition temperature of the reactants and the product. The auto-ignition temperature is defined as that minimum temperature required to initiate or cause self-sustained combustion independently of the heating or heated element.[28] Compounds having low auto-ignition temperature would require better heat removal. The use of high excess air again provides a method of realizing adequate heat removal.

2.4 STATISTICAL ANALYSIS OF AIR OXIDATION PROCESSES

In this section, results of statistical analysis of existing air oxidation processes are presented. The purpose of the analysis is to develop a nationwide VOC emission profile. The analysis was based on the

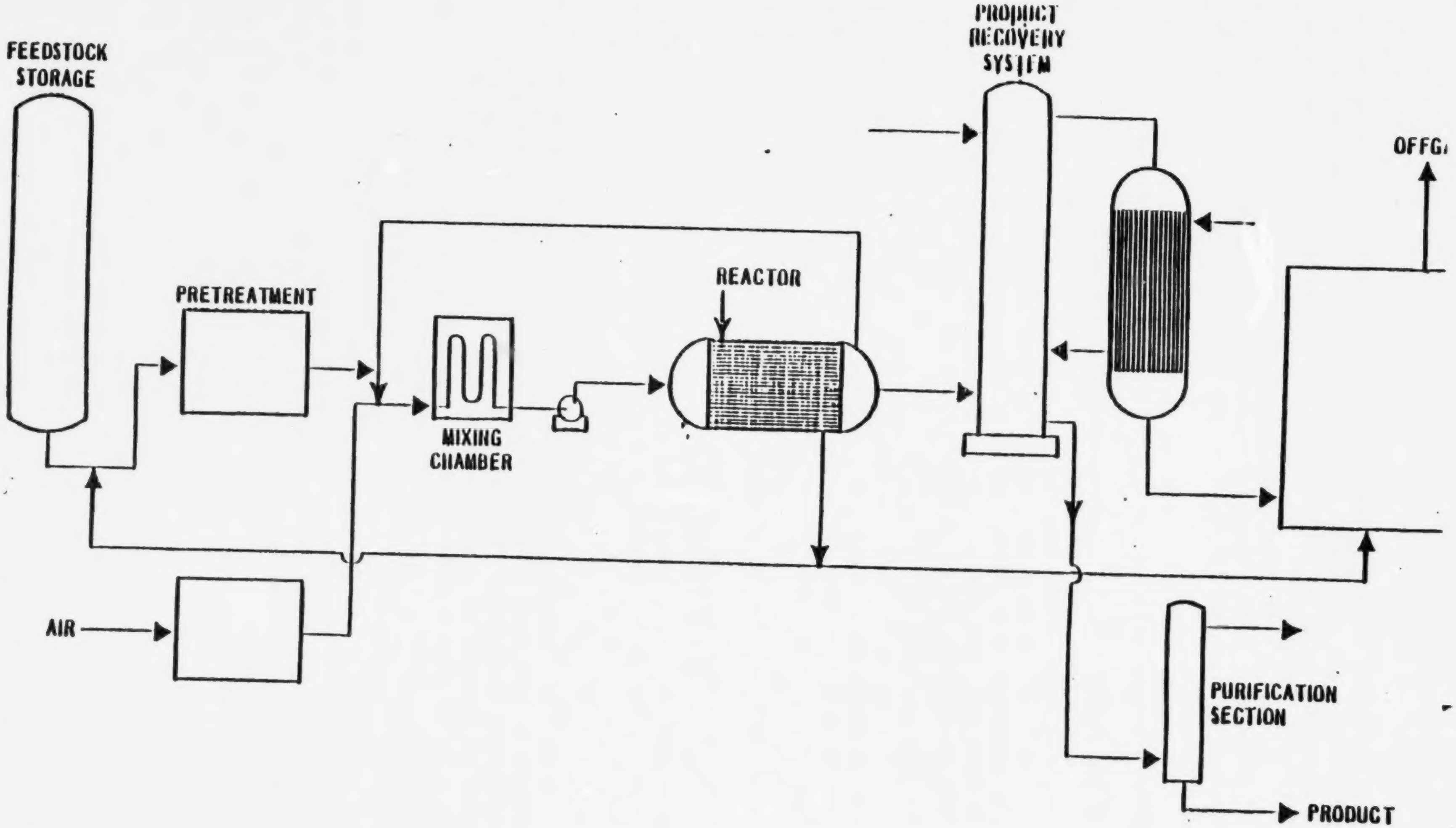

FEEDSTOCK STORAGE
PRETREATMENT
AIR
MIXING CHAMBER
REACTOR
PRODUCT RECOVERY SYSTEM
OFFG
PURIFICATION SECTION
PRODUCT

Figure 2-2. Schematic of a flowsheet for a vapor phase air oxidation process.

data collected from 59 plants producing 14 SOCMI chemicals by air oxidation processes. The details of the statistical procedure and the analysis of the data are presented in Appendix B. The following are the conclusions of the statistical analysis.

1. Of the 14 SOCMI chemicals included in the data base, one chemical is produced in both liquid and vapor phase, while of the remaining 13 chemicals, eight are produced in the vapor phase and five in the liquid phase.

2. The ratio of excess air to the stoichiometric air requirement for vapor phase oxidation processes ranges from less than one to 13.

3. All liquid phase reactions examined have the ratio of excess air to the stoichiometric air requirement of less than three.

4. Excess air requirement is influenced by reaction stoichiometry, reaction temperature, auto-ignition temperatures, and explosive limits.

5. Of the 44 plants producing SOCMI chemicals in the vapor phase, the distribution of flows, VOC, and heat content shows that 35 plants have streams with less than 1.0 volume percent VOC; 38 plants have flows less than 50,000 scfm and 19 plants have streams with less than 20 Btu/scf heat content. The maximum VOC content is 2.2 volume percent, the maximum flow is 117,000 scfm, and the maximum heat content is 122.55 Btu/scf.

6. Of the 15 plants producing SOCMI chemicals in the liquid phase, the distribution of flows, VOC, and heat content shows that nine plants have streams with less than 0.1 volume percent VOC, seven plants have flow less than 10,000 scfm, and 14 plants have streams with less than 20 Btu/scf heat content. The maximum VOC content is 0.76 volume percent, the maximum flow is 60,000 scfm, and the maximum heat content is 43.8 Btu/scf.

2.4.1 National Emission Profile

Air oxidation facilities use 36 types of oxidation processes (23 principal processes and 13 specialty processes) to manufacture 36 different organic chemicals. Because of the number and diversity of facilities and processes in the air oxidation industry, a chemical-by-chemical development of CTG's would require large amounts of time, effort, and money. A unit process approach, on the other hand, allows development of a CTG that provides for regulatory development for VOC emissions from all SOCMI air oxidation processes. This unit process approach allows the resource-efficient statistical estimation of the RACT impacts for VOC emissions control from all air oxidation processes.

In the unit process approach, no model plants are used for impact analysis. Rather, the information concerning existing air oxidation facilities is analyzed statistically and used to construct a national profile. This national profile replaces the traditional model plant and can be considered a statistical model of SOCMI air oxidation processes and facilities. The national profile characterizes air oxidation processes according to national distributions of key variables (e.g., vent gas stream flowrate, net heating value, hourly VOC emissions, and whether the offgas contains halogenated compounds) that can be used to determine VOC emissions and the cost and energy impacts associated with RACT. RACT is therefore examined as a percent VOC emission reduction based on thermal oxidation as the single control technique. The RACT impacts are evaluated as impacts upon the entire population of affected facilities.

The actual use of the national statistical profile assumes that the distribution of offgas flowrate, hourly emissions, net heating value, and corrosion properties is chemical independent. Chemical identities are not considered in the profile, nor is there claimed to be a one-to-one correspondence between any one data vector and an existing offgas stream. It is assumed, however, that the overall proportions and distributions of the parameter values and data vectors be similar to those of the existing population of air oxidation facilities. Thus, since the national statistical profile contains 59 data vectors, each data vector and associated impacts of population control represents 1/59 of the existing population to be analyzed for control.

The national emission profile was constructed using emissions data from the Houdry questionnaire.[29] The questionnaire covered 14 major air oxidation chemicals. These chemicals are shown in Table 2-11. A total of 59 air oxidation plants are represented by the Houdry data, which is about 36 percent of the total air oxidation plants in existence today.

TABLE 2-11. CHEMICALS COVERED BY HOUDRY QUESTIONNAIRE

Chemical	Process	Number of Plants
Acetaldehyde	Ethanol	1
	Ethylene	1
Acetic Acid	Butane	1
Acrylonitrile	Propylene	4
Cyclohexanone/Cyclohexanol	Cyclohexane	3
Dimethyl Terephthalate	p-Xylene, Methanol	2
Ethylene Dichloride	Oxychlorination	9
Ethylene Oxide	Ethylene	4
Formaldehyde	Methanol Silver Catalyst	9
Formaldehyde	Methanol Mixed Metal	4
Hydrogen Cyanide	Ammoxidation Methane	1
Maleic Anhydride	Benzene	7
Phenol	Cumene	6
Phthalic Anhydride	Naphthalene	2
	o-Xylene	3
Terephthalic Acid	p-Xylene	2

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3. EMISSION CONTROL TECHNIQUES

3.1 INTRODUCTION

This chapter describes the control techniques and associated emission reduction effectiveness for air oxidation unit process vents of the synthetic organic chemical manufacturing industry (SOCMI). The effectiveness of combustion systems is examined with respect to their principles of operation, advantages, and disadvantages.

The SOCMI process vent streams show a great variety in volume flows, chemical compositions, and volatile organic compound (VOC) concentrations. This chapter concentrates on thermal oxidation since it is a VOC control method universally applicable to SOCMI air oxidation vent streams, although it is not necessarily the best for a given process.

Effectiveness and specificity of condensers, absorbers, adsorbers, and catalytic oxidizers may be affected by changes in waste stream conditions. These conditions include flowrate, VOC concentration, chemical and physical properties of VOC, waste stream contaminants, and waste stream temperature. Analysis of air oxidation VOC emissions control by these methods would be unwieldy. Also, control systems based on condensation or absorption are generally used as product recovery devices, and the removal efficiencies decrease as the VOC concentrations decrease.

Thermal oxidation, however, is much less dependent on process and waste stream conditions than the other control techniques. It is the only demonstrated VOC control which is applicable to all SOCMI air oxidation processes. Incinerator cost and efficiency determinations require a limited amount of waste stream data (volume flow, hourly emissions, net heating value, and corrosive properties). The choice of thermal oxidation as the single control technique for analysis yields conservative estimates of energy, economic, and environmental impacts since thermal oxidation is relatively expensive and energy-intensive.

All new incinerators can achieve at least a 98 percent VOC reduction or 20 ppmv exit concentration, whichever is less stringent. This control level can be achieved by incinerator operation at conditions which include a maximum of 1600°F and 0.75 second residence time.

Process modification, improvements in product recovery, and use of additional control devices are possible routes to lower emission levels. This chapter discusses the advantages and disadvantages of using product recovery devices such as absorbers, adsorbers, and condensers alone, or in conjunction with VOC control devices such as boilers and thermal and catalytic oxidizers to achieve reduction of VOC emissions. Detailed descriptions and efficiency data are available in Appendix A and in the references.

Boilers can be useful as VOC control devices only when the waste gas stream volume flow is not large enough to upset the combustion process. Furthermore, the waste gas stream must either have sufficient oxygen to be used as combustion air or have a sufficiently high heating value to be used as part of the fuel input. The only air oxidation process which currently employs a boiler or process heater for VOC control is the Andrussow process for manufacture of hydrogen cyanide.

All air oxidation processes use a combination of absorption devices, condensers, or carbon adsorption units for product recovery (or for recovery of unreacted raw material). These devices are usually designed to recover only as much of the VOC as is economically feasible and therefore would not be considered control devices. However, in some plants, these devices are designed to remove more than that amount which is economically justified. In this case, the devices operate both for product recovery and as control devices for emission reduction or to reduce the pollutant load on some other final control device.

Table 3-1 shows some of the SOCMI air oxidation chemical processes and the product recovery-VOC emission control methods used.

3.2 ADSORPTION

The main function of vapor-phase carbon adsorption is to contain and concentrate dilute organic vapors from waste streams where condensers or absorbers are ineffective or uneconomical. Carbon adsorption in most cases is used for recovery of expensive, unreacted raw material and not for VOC emission control. The major application of carbon adsorption in air oxidation processes is for the recovery of aromatic feedstocks such as benzene, xylene, and cumene. Selected air oxidation processes known to employ carbon adsorption are listed in Table 3-2.

Adsorption devices work by capturing vapor-phase molecules upon the surface of a solid. The molecules adhere primarily through two mechanisms: (1) physical adsorption, in which Van der Waal's forces attract and hold the gas molecules to the adsorbent surface. and (2) chemical adsorption (chemisorption), in which the molecules are chemically bonded to the adsorbent.[1]

Oxygenated adsorbents such as silica gels, fullers, diatomaceous, and other siliceous earths, synthetic zeolites, and metallic oxides exhibit greater selectivity than activated carbon. However, due to their affinity for polar molecules, they have a greater preference for water than organics and are of little use on the moist air streams from SOCMI air oxidation process vents.[2] Vent stream dehumidification may be possible but will necessitate more equipment and increase treatment cost.

3.2.1 Carbon Adsorption Process

Material recovery by carbon adsorption may be too difficult or expensive for some chemicals when their vapor concentrations are below 700 ppmv.[3] Although carbon adsorption system configurations vary according to the volume of gas handled and allowable pressure drop, a typical set-up is shown in Figure 3-1. After filtering and cooling, the waste gas is directed through a bed of carbon granules (Adsorber 1). In time, traces of organic vapors appear in the exit air and the removal efficiency rapidly decreases (breakthrough). At this point, the waste gas stream is routed through a fresh bed, and the saturated bed is regenerated by passing a hot gas through it to desorb (strip) the organics from the carbon. Low-pressure steam is a common regeneration fluid providing a concentration gradient to facilitate mass transfer of adsorbate from the carbon bed and supplying the heat of desorption. The steam and organic vapors are then condensed and the

TABLE 3-1. PRODUCT RECOVERY AND EMISSION CONTROLS CURRENTLY USED IN ONE OR MORE PLANTS EMPLOYING MAJOR AIR OXIDATION PROCESSES

Chemical	Process	Product or Raw Material Recovery Equipment	Emission Control Equipment
Acetaldehyde	Wacker	1, 2	
Acetic Acid	Wacker	1, 2	
Acetic Acid/Formic Acid/Methyl Ethyl Ketone	Butane	1, 2	
Acetone/Phenol	Cumene Peroxidation	1, 3	
Acrylonitrile	Propene Ammoxidation	1, 2	5
Acrylic Acid	Propene	1, 2	4B
1,3-Butadiene	Butene Oxidative Dehydrogenation	1, 2	4B
Cyclohexanol/Cyclohexanone	Cyclohexane	1, 2	
Ethylene Dichloride	Ethylene Oxychlorination	1, 2	4B, 5
Ethylene Oxide	Ethylene	1, 2	5
Formaldehyde	Silver Catalyst	1, 2	
Formaldehyde	Mixed Metal Oxide Catalyst	1, 2	
Hydrogen Cyanide	Andrussow	2	6
Maleic Anhydride	Benzene	1, 2, 3	4B, 5
Maleic Anhydride	Butane	1, 2	4
Phthalic Anhydride	Naphthalene	1, 2	4
Phthalic Anhydride	Xylene	1, 2	4B
Propylene Oxide/Styrene	Ethylbenzene Peroxidation	1, 2	
Terephthalic Acid/Dimethyl Terephthalate	Xylene	1, 2, 3	

KEY:

1 Condenser
2 Absorber
3 Carbon Adsorber
4 Thermal Incineration
4B Thermal Incinerator - Waste Heat Boiler
5 Catalytic Incinerator
6 Process Heater or Boiler

TABLE 3-2. SELECTED AIR OXIDATION PROCESSES KNOWN TO USE CARBON ADSORPTION FOR PRODUCT/RAW MATERIAL RECOVERY OR EMISSION REDUCTION

Chemical	Primary Compound Recovered
Acetone/Phenol	Cumene
Maleic Anhydride	Benzene
Terephthalic Acid/ Dimethyl Terephthalate	Xylene

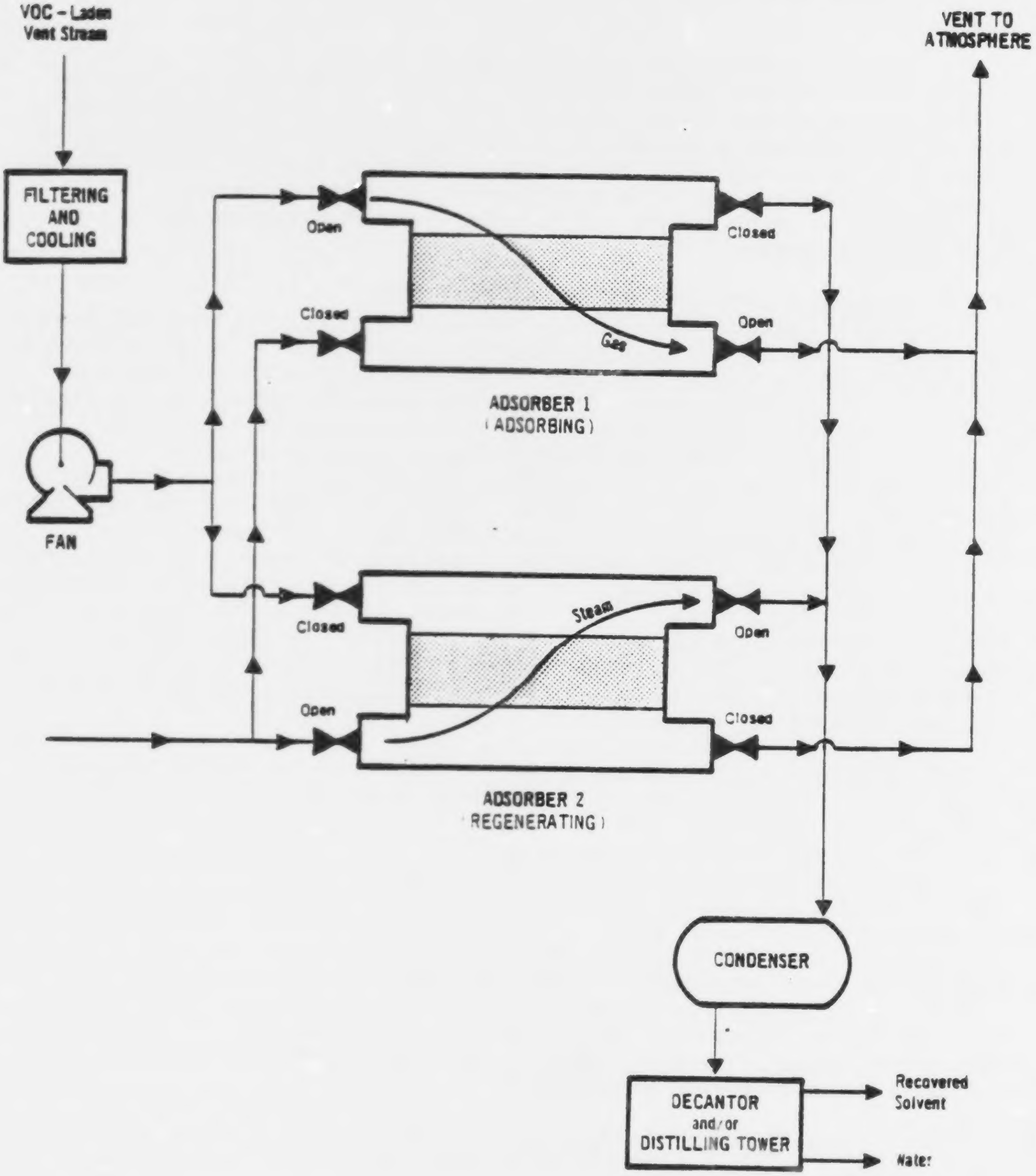
VOC - Laden Vent Stream
FILTERING AND COOLING
FAN
VENT TO ATMOSPHERE
Open
Closed
Closed
Open
Gas
ADSORBER 1 (ADSORBING)
Closed
Open
Steam
Open
Closed
ADSORBER 2 (REGENERATING)
CONDENSER
DECANTOR and/or DISTILLING TOWER
Recovered Solvent
Water

Figure 3–1. Two stage regenerative adsorption system.

organics separated from the water by decantation and/or distillation. The freshly-regenerated bed is cooled, dried, and prepared for another service cycle.

3.2.2 Carbon Adsorption Emissions Removal Efficiency

State-of-the-art carbon adsorption systems for VOC recovery can have outlet concentrations in the range of 50 to 100 ppmv with concentrations as low as 10 to 20 ppmv achievable with some compounds.[4] For inlet concentrations from 700 to 5000 ppmv, these numbers yield an expected VOC adsorption removal efficiency range of 86 to 99 percent. Adsorption removal efficiencies up to 95 percent can be achieved from some chemicals in well designed systems.[5]

3.2.3 Parameters Affecting VOC Removal Efficiency

The most important operating parameter affecting continuing VOC removal efficiency is the amount of steam used for regeneration. The graph given as Figure 3-2 shows a generalized form of the relationship of effluent VOC concentration to steam usage. The exact relationship depends on the type of VOC being removed and on the operating characteristics of the system. Figure 3-2 shows that reduced effluent concentration is obtained by increasing the steam ratio and that very low effluent concentration levels may be obtained with high steam ratio. Figure 3-2 shows that the position of the effluent concentration curve for each particular compound is a function of the adsorption temperature, regeneration temperature, and carbon loading capacity. The effluent concentration curve is relatively independent of inlet VOC concentrations. When the adsorption temperature increases, the effluent concentration curve baseline may increase. Higher regeneration temperatures may shift the effluent outlet concentration curve downward. A different loading capacity may shift the curve laterally, since different amounts of steam may be required to regenerate the carbon.[6]

VOC with molecular weights below 45 do not adsorb well on carbon; high (>130) molecular weight VOC are more difficult to remove during regeneration.[7] Also, during adsorption of multicomponent gas streams, the higher boiling point components tend to displace the lower boiling point components from the adsorption sites on the carbon.[8]

Adsorption rates decrease sharply for gas streams with temperatures of 38°C (100°F) and above.[9,10] Inlet VOC concentrations may be limited to 25 percent of LEL (.5000 ppmv) by insurance requirements. Although some moisture is desirable in the waste gas to help dissipate the heat of adsorption and provide more uniform bed temperatures, excessive humidity can adversely affect the VOC removal efficiency of a carbon adsorption system. Mist in the gas stream can rapidly saturate an adsorption bed, taking up adsorption sites. Operating capacity decreases become pronounced at relative humidities over 50 percent.[11]

3.2.4 Factors Affecting Applicability and Reliability

Although carbon adsorption can be used for product recovery and to help control VOC emissions, it is not a control method generally applicable to SOCMI air oxidation processes. The vent streams from some of these

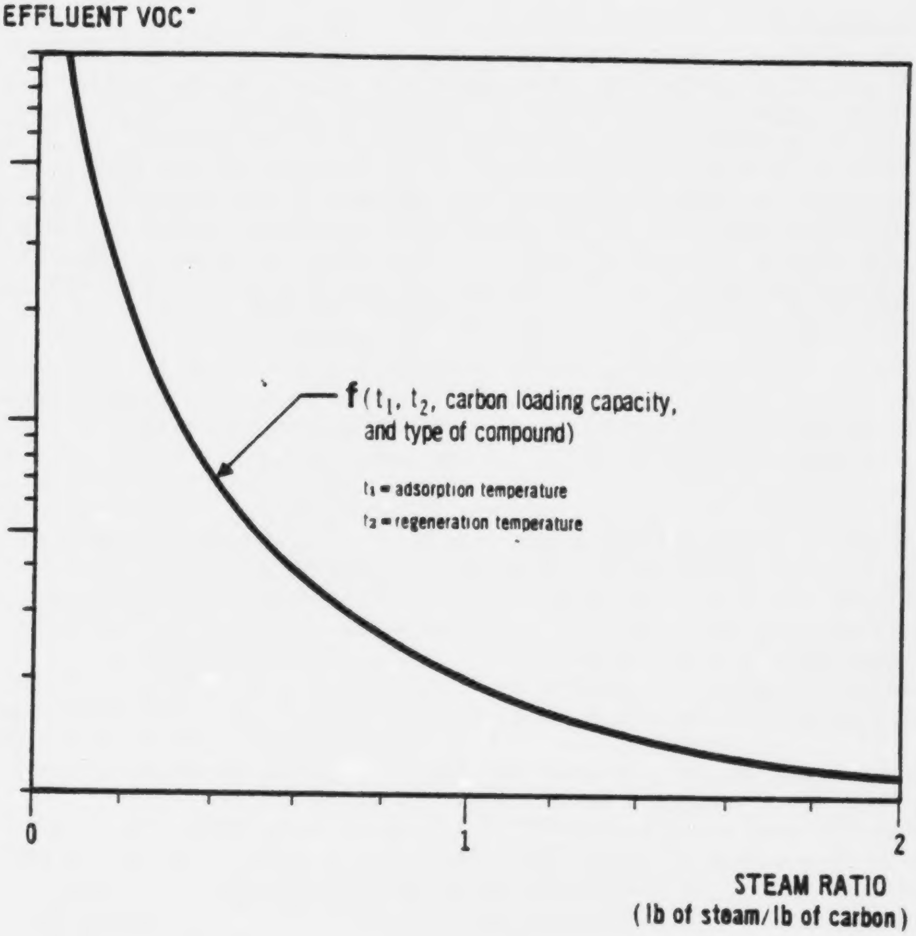

Figure 3–2. Generalized form of the relationship of effluent VOC concentration to steam usage.

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* Due to the generalized nature of the relationship, the axis is not numbered. However, it is marked off in a logarithmic scale.

processes are often saturated with moisture. This would result in serious loss of adsorption capacity due to the water saturating the adsorbing medium and taking up adsorption sites. Such process vent streams require dehumidification to lower the water content. Process upsets which increase vent stream VOC composition are not uncommon in air oxidation processes, and may result in an excessive temperature rise due to the accumulated heat of adsorption of the extra VOC loading.

3.3 ABSORPTION

Absorption is one of the two primary methods of product recovery used in air oxidation processes. Absorbers are also commonly applied as auxiliary control devices prior to combustion devices. An absorber can be added to an existing process for the purpose of VOC control, or an existing absorber could be modified, perhaps by an increase in the size or a decrease in the operating temperature, for the purpose of VOC control. Some of the air oxidation processes which employ absorption are listed in Table 3-3.

Gas absorption devices work by dissolving the soluble components of a gaseous mixture in a liquid. Absorption may only entail the physical phenomenon of solution or may also involve chemical reaction of the solute with constituents of the solution.[12] The absorbing liquids (solvents) used are chosen for high solute (VOC) solubility and include liquids such as water, mineral oils, non-volatile hydrocarbon oils, and aqueous solutions of oxidizing agents like sodium carbonate and sodium hydroxide.[13] Devices based on absorption principles include spray towers, venturi scrubbers, packed columns, and plate columns. Spray towers require high pressure to obtain droplets ranging in size from 500 to 1000 mm in order to present a sufficiently large surface contact area.[14] They can remove particulate matter without plugging, but have the least effective mass transfer capability and thus, are restricted to particulate removal and control of high-solubility gases such as sulfur dioxide and ammonia.[15] Venturi scrubbers have a high degree of gas-liquid mixing and high particulate removal efficiency but require high pressure and have relatively short contact times, so their use is also restricted to high-solubility gases.[16] The choice for gas absorption is thus between packed and plate columns. Packed columns are mostly used for handling corrosive materials and liquids with foaming or plugging tendencies. They are less expensive than plate columns for small-scale or pilot plant operations where the column diameter is less than 0.6 m (2 ft). Plate columns are preferable for large-scale operations, where internal cooling is desired and where low liquid flowrates would inadequately wet the packing.[17]

3.3.1 Absorption Process

The mechanism of absorption consists of the selective transfer of one or more components of a gas mixture into a solvent liquid. The transfer consists of diffusion to the solvent and dissolution into it. For any given solvent, solute, and set of operating conditions, there exists an equilibrium ratio of solute concentration in the gas mixture to concentration in the solvent.[18] The driving force for mass transfer at a given point in the operating tower is related to the difference between the actual concentration ratio and the equilibrium ratio.[19]

TABLE 3-3. SELECTED AIR OXIDATION PROCESSES KNOWN TO USE ABSORPTION FOR PRODUCT RAW MATERIAL RECOVERY OR EMISSIONS REDUCTION

Chemical
Acetaldehyde
Acetic Acid/Formic Acid/MEK
Acrylonitrile
Acrylic Acid
1,3-Butadiene
Cyclohexanol/Cyclohexanone
Ethylene Dichloride
Ethylene Oxide
Formaldehyde
Hydrogen Cyanide
Maleic Anhydride
Phthalic Anhydride
Propylene Oxide/Styrene
Terephthalic Acid/Dimethyl Terephthalate

A schematic of a packed, gas absorption tower is shown in Figure 3-3. The waste gas of VOC concentration y_{A0} enters at the bottom and rises through the packing, contacting the absorbing liquid on the surface of the packing material. The VOC (solute) is dissolved in the absorbent liquid (solvent) and is discharged at the bottom of the tower for recovery or disposal. The cleaned gas exits at the top with reduced VOC concentration y_{A1}, ready for release or final treatment such as incineration.

3.3.2 Absorption VOC Removal Efficiencies

Systems that utilize organic liquids as solvents usually include the stripping and recycling of the solvent to the absorber. In this case the VOC removal efficiency of the absorber is dependent on the solvent stripping efficiency. If, for example, a system achieved a removal efficiency in excess of 99 percent with once-through solvent usage, it would be expected that the removal efficiency would drop to about 94 percent with solvent recycling.[20] Once-through solvent usage can create a liquid waste problem and incur additional treatment costs.

For a given absorbent and absorbate, an increase in absorber size or a decrease in the operating temperature can increase the VOC removal efficiency of the system. It may be possible in some cases to increase VOC removal efficiency by a change in the absorbent.

3.3.3 Factors Affecting Efficiency and Reliability

The effectiveness of an absorption tower, which is the rate of mass transfer between the two phases, is largely dependent upon the available gas-liquid contact area. In packed towers, a reduction in the liquid-to-gas ratio can lead to channeling where some of the packing is not wetted by the liquid. Excessive gas flowrates can increase the liquid holdup until the tower floods and liquid exists at the top with the gas.

VOC concentration can affect the operation of absorption equipment. Excessive VOC loading can raise the temperature of the tower due to increased rate of release of the heat of solution, resulting in a decreased concentration gradient. Absorption is usually not considered when the VOC concentration is below 200-300 ppmv.[21]

3.4 CONDENSATION

Condensation is one of the two primary methods of product recovery used in air oxidation processes. Condensers are also commonly applied as auxiliary control devices before thermal incinerators, adsorbers, and other control devices.[22] An existing condenser can be modified for improved VOC emission control by lowering the operating temperature. The suitability of condensation as an emissions control method depends on several parameters. These include the VOC concentration at the inlet (usually >1 percent), the VOC removal efficiency required, the VOC recovery value, and the size of the condenser required for handling the gas volume flowrate.[23] Air oxidation processes which employ condensation are listed in Table 3-4.[24]

Condensation devices are usually surface or contact condensers.[25] Contact condensers spray a cooled liquid directly into the gas stream, also acting as scrubbers in removing normally noncondensable vapors.[26] The

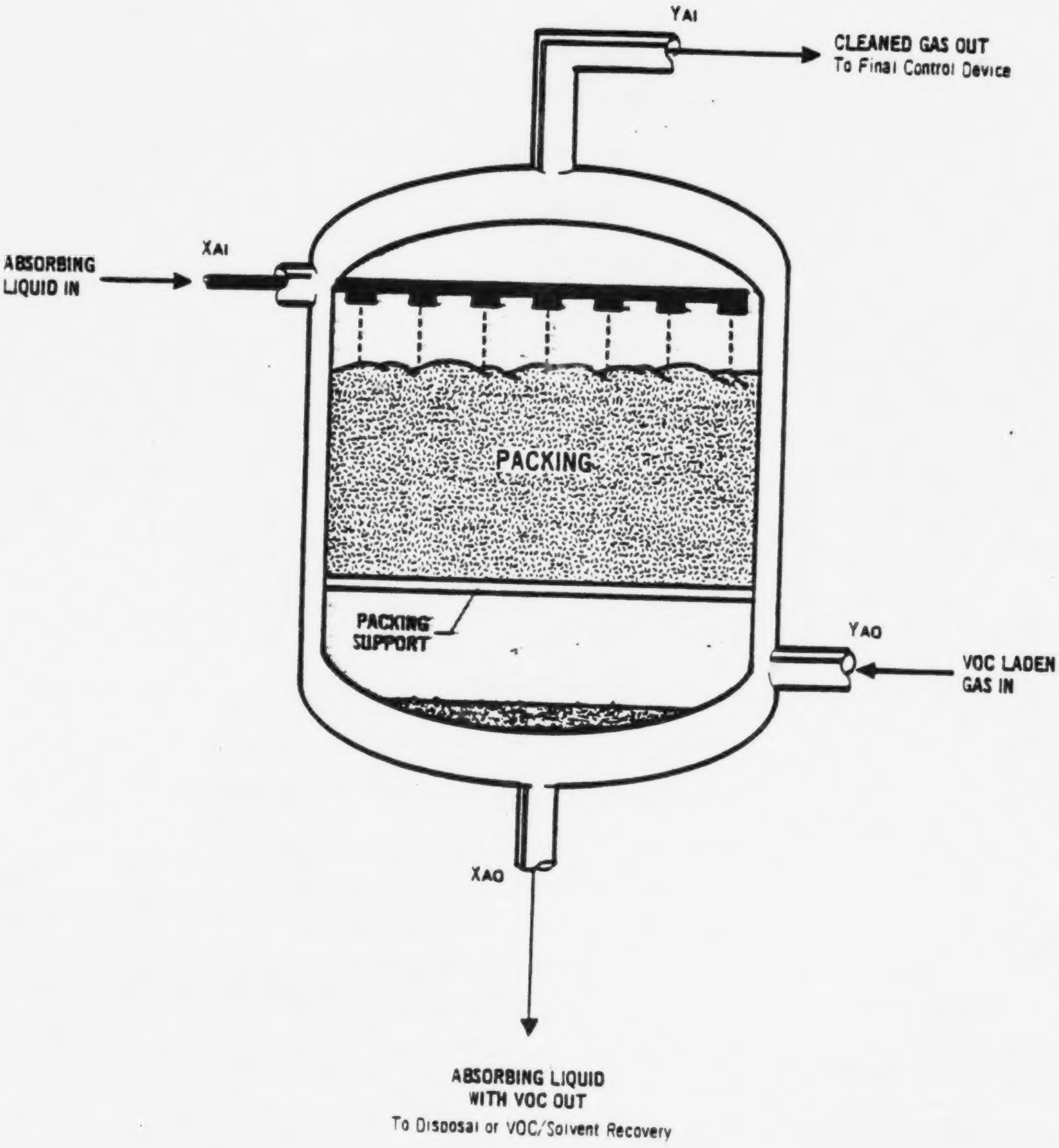
YAI
CLEANED GAS OUT
To Final Control Device
ABSORBING
LIQUID IN
XAI
PACKING
PACKING
SUPPORT
YAO
VOC LADEN
GAS IN
XAO
ABSORBING LIQUID
WITH VOC OUT
To Disposal or VOC/Solvent Recovery

Figure 3–3. Packed tower for gas absorption.

TABLE 3-4. SELECTED AIR OXIDATION PROCESSES KNOWN TO USE CONDENSATION FOR PRODUCT/RAW MATERIAL RECOVERY OR EMISSIONS REDUCTION

Chemical
Acetaldehyde
Acetic Acid/Formic Acid/MEK
Acetone/Phenol
Acrylonitrile
Acrylic Acid
1,3-Butadiene
Cyclohexanol/Cyclohexanone
Ethylene Dichloride
Ethylene Oxide
Formaldehyde
Maleic Anhydride
Phthalic Anhydride
Propylene Oxide/Styrene
Terephthalic Acid/Dimethyl Terephthalate

coolant is usually water or perhaps a process feed stream.[27] Contact condensers are generally cheaper, more flexible and efficient for VOC removal. However, the spent coolant can present a secondary emissions source or waste water treatment problem.[28] Surface condensers have more auxiliary equipment but can recover valuable and marketable VOC. They do not contaminate the coolant, therefore minimizing waste disposal problems. Only surface condensers are discussed in this section.

3.4.1 Condensation Process

Condensation occurs when the partial pressure of a condensable component equals its vapor pressure at that temperature. Most surface condensers are of the shell-and-tube type and achieve condensation by removing heat from vapors.[29] As the coolant passes over the tubes, the VOC vapors condense inside the tubes and are recovered. The coolant used depends upon the saturation temperature (dewpoint) of the VOC. Chilled water can be used down to 7°C (45°F), brines to -34°C (-30°F), and freons below -34°C (-30°F).[30] Temperatures as low as -62°C (-80°F) may be necessary to obtain the required VOC removal efficiencies.[31] A table of the estimated operating temperature required to achieve a given VOC removal efficiency is given in Reference 31. These temperatures were estimated for aliphatic and halogenated aliphatic hydrocarbons as a function of inlet VOC concentration.

The major pieces of equipment of a condenser system (as shown in Figure 3-4) are the shell-and-tube heat exchanger (condenser), refrigeration system (coolant supply), storage tanks, and pumps.

3.4.2 Condenser VOC Removal Efficiency

VOC removal efficiencies of 50 percent are typical of a condenser used in conjunction with other control devices. The maximum efficiency reported is close to 95 percent with average efficiencies of 80 percent reported in the literature.[32]

3.4.3 Parameters Affecting Reliability and Efficiency

Condensers used for VOC control often operate at temperatures below the freezing point of water. This requires that moist vent streams, such as those found in air oxidation processes, be dehumidified before VOC removal to prevent the formation of ice in the condenser. Particulate matter must not be allowed to enter a surface condenser system since it may deposit on the finned tubes and interfere with gas flows and heat transfer. Gas flowrates from 100 to 2000 cfm are representative of the capacity range for condensers as emission control devices. Vent streams containing less than one-half percent VOC are generally not considered for control by condensation.[33]

3.5 CONTROL BY COMBUSTION TECHNIQUES

Combustion control techniques result in the destruction of the raw material or product present in the offgas. Therefore, they are usually to be considered add-on emission control techniques. Although the process material can never be recovered, it is possible to recover much of the

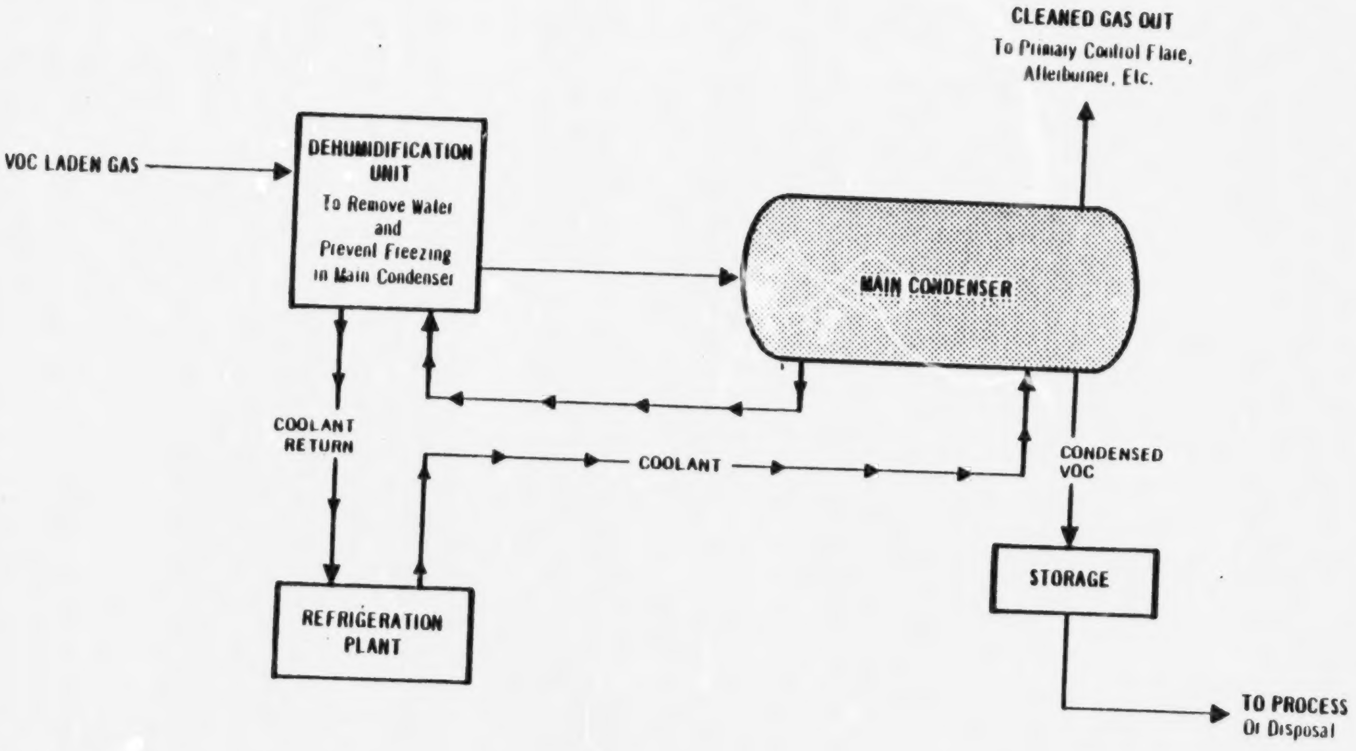
CLEANED GAS OUT
To Primary Control Flare, Afterburner, Etc.
VOC LADEN GAS
DEHUMIDIFICATION UNIT
To Remove Water and Prevent Freezing in Main Condenser
MAIN CONDENSER
COOLANT RETURN
COOLANT
CONDENSED VOC
STORAGE
REFRIGERATION PLANT
TO PROCESS
Or Disposal

Figure 3–4. Condensation system.

thermal energy released by combustion. In the case of offgas with a high heating value, it may be economically attractive to combust the vent stream in a boiler or process heater.

3.5.1 General Combustion Principles

Combustion is a rapid, exothermic oxidation process which results in the complete or incomplete oxidation of VOC. Most fuels and VOC contain carbon and hydrogen which, when burned to completion with oxygen, form carbon dioxide and water.

Since air oxidation vent streams generally contain little oxygen, additional combustion air must be provided. The total gas volume flow is therefore relatively larger than that associated with other types of control.

3.5.2 Combustion Control Devices

Control devices using combustion principles include furnaces, boilers, and thermal and catalytic oxidizers. Combustion in thermal and catalytic oxidizers are the usual control methods for air oxidation processes.

Furnaces and boilers are only occasionally used as control devices for the larger air oxidation vent streams because the fuel requirements of their firing cycles may not coincide with the availability or heating value of the offgas. Waste streams with large flows and low heating values can adversely affect the operation of these devices in two ways. By lowering furnace temperatures, they cause incomplete combustion and diminished steam production. Furthermore, an increased volume flow of gases can exceed the handling capabilities of the exhaust system.

Catalytic oxidizers are not widely used because the catalysts can be poisoned by sulfur- and halogen-containing compounds. Moreover, increases of VOC concentration in poorly controlled streams can raise the catalyst bed temperature excessively to the point of deactivating the catalyst.

3.5.3 Thermal Oxidizers

Thermal oxidation is the method of VOC emission control most widely used for air oxidation processes because it is applicable to a variety of chemicals and vent streams conditions. Incineration is the usual method of pollution control for waste streams with combustible concentration below the LEL (about 470 $\frac{\text{kcal}}{\text{Nm}^3}$ or 53 $\frac{\text{Btu}}{\text{scf}}$) such as those found in SOCMI air oxidation processes.[34] Table 3-5 is a partial listing of chemical processes using thermal oxidation for VOC control.

Thermal oxidizers can also control halogenated VOC. However, a higher chamber temperature is required to properly oxidize chlorinated hydrocarbons and convert the noxious combustion products to a form more readily removable by flue gas scrubbing.

3.5.3.1 Thermal Oxidation Process. The combustion process is influenced by time, mixing, and temperature. An efficient thermal oxidizer must provide:

1. A chamber temperature high enough to enable the oxidation reaction to proceed rapidly to completion,

TABLE 3-5. PARTIAL LIST OF AIR OXIDATION CHEMICALS USING THERMAL OXIDIZER FOR CONTROLLING VOC EMISSIONS FROM OFFGAS STREAM

Chemical	Number of Plants Reported	Reported Operating Temperature (°F)	Reported Efficiency
Butadiene	1[a]	Not Reported	Not Reported
Acrylic Acid	3[b]	Not Reported	Not Reported
Acrylonitrile	2[c]	1800	>99%[c]
Formaldehyde	4[d]	2000	99.8-100%[d]
Phthalic Anhydride	1[e]	1200	90-95%
Maleic Anhydride	3[f]	1400	93%
Maleic Anhydride	3[f]	1600	99%

[a] Standifer, R.L. Butadiene Product Report. I.T. Enviroscience. EPA-450/3-80-028e.

[b] Blackburn, J.W. Acrylic Acid and Esters Report. I.T. Enviroscience. EPA-450/3-80-028e.

[c] Hobbs, F.D. and Key, J.A. Acrylonitrile Product Report. I.T. Enviroscience. EPA-450/3-80-028e.

[d] Lovell, R.J. Formaldehyde Product Report. I.T. Enviroscience. EPA-450/3-80-028d.

[e] Office of Air and Waste Management. U.S. Environmental Protection Agency. Research Triangle Park, NC. Control Techniques for Volatile Organic Emissions from Stationary Sources. Publication No. EPA-450/2-78-022. May 1978.

[f] Lawson, J.F. Maleic Anhydride Product Report. I.T. Enviroscience. EPA-450/3-80-028a.

2. Enough turbulence to obtain good mixing between the hot combustion products from the burner, combustion air, and VOC, and

3. Sufficient residence time at the chosen temperature for the oxidation reaction to reach completion.

Combustion chamber temperature is an important parameter in the design of a thermal oxidizer since oxidation rates are highly temperature-dependent. Incineration of low heating value offgas necessitates the burning of an auxiliary fuel to achieve the desired chamber temperature. Destruction of most VOC occurs rapidly at temperatures over 760°C (1400°F). However, higher temperatures, on the order of 980°-1100°C (1800°-2000°F), may be required when incinerating halogenated VOC.

Mixing is crucial in achieving good thermal oxidizer performance. A properly designed incinerator rapidly combines the offgas, combustion air, and hot combustion products from the burner. This ensures that the VOC be in contact with sufficient oxygen at a temperature high enough to start the oxidation reaction. Improper mixing can permit packets of waste gas to pass through the incinerator intact. Poor mixing can also lead to poor temperature distributions so that not all the waste gas stream reaches or remains at the design combustion temperature.

Residence time is the time available for the oxidation reaction to occur within the combustion chamber. Residence times from as low as 0.3 to several seconds have been used in thermal oxidizer design.[35] Vendors generally define residence times in one of two ways. Some count offgas residence time in any of the available volume of the combustion chamber. Others credit only residence time within that volume in which the flue gas is at the combustion temperature. It is this volume which is theoretically related to destruction efficiency. Therefore, incinerator efficiency data which use the latter definition of residence time are more easily compared in an analysis of the relationship of destruction efficiency to residence time. Moreover, according to this definition, a larger combustion chamber is required to achieve a given residence time. Therefore, this definition yields more conservative estimates of the cost of control.

Other parameters affecting oxidizer performance are offgas heating value, water content, and excess combustion air. The offgas heating value is a measure of the heat available from the combustion of the VOC in the offgas to CO_2 and H_2O. The heat of combustion for specific organic compounds can range from 950 $\frac{KJ}{Nm^3}$ (25 $\frac{Btu}{scf}$) for carbon tetrachloride (CCl_4) to 35,700 $\frac{KJ}{Nm^3}$ (960 $\frac{Btu}{scf}$) for methane (CH_4).[36] Incineration of offgas with a low heating value (less than 1860 $\frac{KJ}{Nm^3}$ (50 $\frac{Btu}{scf}$)) may require the burning of an auxiliary fuel to maintain the desired combustion temperature. Auxiliary fuel requirements can be lessened or eliminated by the use of recuperative heat exchangers. Offgas with a heating value above 1860 $\frac{KJ}{Nm^3}$ (50 $\frac{Btu}{scf}$) may support combustion but may need auxiliary fuel for flame stability. Combustion of an offgas with a heating value over 5200 $\frac{KJ}{Nm^3}$ (140 $\frac{Btu}{scf}$) can result in flame temperatures in excess of 1200°C (2200°F). Conventional oxidation equipment can only be used for such streams if the temperature is kept below 1200°C (2200°F) by addition of air, water vapor, or liquid water or circulation of exhaust gas.[36]

A thermal oxidizer handling offgas streams with varying heating values requires adjustment to maintain the proper chamber temperatures and operating efficiency. Water has a heat of vaporization of 41,390 (KJ/(kg mol) (18,000 $\frac{\text{Btu}}{\text{lb mol}}$) and a heat capacity of about 27.5 $\frac{\text{KJ}}{\text{kg mol °C}}$ (11.8 $\frac{\text{Btu}}{\text{lb mol °F}}$ at 870°C (1600°F) and 101 kPa (14.7 psia).[37] Entrained water droplets in an offgas stream can substantially increase auxiliary fuel requirements due to the additional energy needed to vaporize the water and raise it to the combustion chamber temperature. Combustion devices are operated with some quantity of excess air to ensure a sufficient supply of oxygen. Too much excess air causes an increase in auxiliary fuel requirements since the extra air is heated up to chamber temperature. Too much excess air also increases the thermal oxidizer's flue gas volume flow rate and, thus, its size and cost.

3.5.3.2 Thermal Oxidizer Design. A thermal oxidizer is usually a refractory-lined chamber containing a burner at one end and generally operated at a temperature of 550°-850°C with a residence time of from 0.3 to one second.[38]

Discrete dual fuel burner(s) and inlets for the offgas and combustion air are so arranged in the chamber to thoroughly mix the hot products from the burners with the offgas and air streams. The mixture of hot reacting gases then passes into the reaction section. This section is sized to allow the mixture enough time at the elevated temperature for the oxidation reaction to reach completion. Energy can then be recovered from the hot flue gases in the heat recovery section. Preheating of combustion air by offgas is a common mode of energy recovery; however, it is sometimes more economical to generate steam. Insurance regulations require that if the waste stream is preheated, the VOC concentration be maintained below 40 percent of LEL to eliminate explosion hazards.

Thermal oxidizers designed specifically for VOC incineration with natural gas as the auxiliary fuel may use a grid-type (distributed) gas burner instead of the conventional dual fuel, forward flame, discrete burners. The tiny gas flame jets on the grid surface ignite the vapors as they pass through the grid and ensure burning of all the vapors at lower chamber temperatures using less fuel and allowing for a shorter reaction chamber.[39] Typical configurations are shown in Figures 3-5 and 3-6.

Thermal oxidizers for halogenated VOC control require additional control equipment. The flue gases are quenched to lower their temperature and routed through absorption equipment such as towers or liquid jet scrubbers to remove the halogenated combustion products.

Packaged, single unit thermal oxidizers can be built to control streams with flowrates in the range of a few hundred scfm to about 50,000 scfm. A typical thermal oxidizer built to handle a VOC waste stream of 850 Nm^3/min (30,000 scfm) at a temperature of 870°C (1600°F) with 0.75 second residence time probably would be a refractory-lined cylinder. Assuming the ratio of flue gas to waste gas is about 2.2, the chamber volume necessary to provide the residence time at that temperature would be about 99 m^3 (3500 ft^3). If the chamber length to diameter ratio is two to one, and allowing a 30.5 cm (1 ft) wall thickness, the thermal oxidizer would measure 8.3 m (27 ft) long by 4.6 m (15 ft) wide, exclusive of heat exchangers and exhaust equipment.

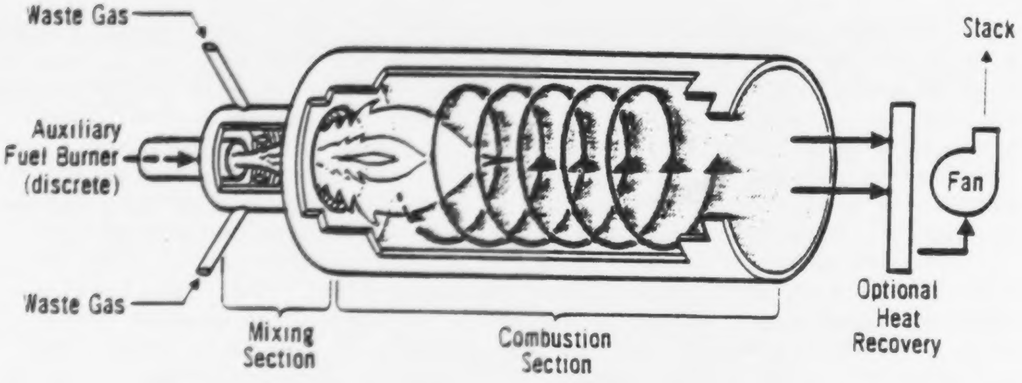
Waste Gas
Auxiliary Fuel Burner (discrete)
Waste Gas
Mixing Section
Combustion Section
Stack
Fan
Optional Heat Recovery

Figure 3–5. Discrete burner, thermal oxidizer.

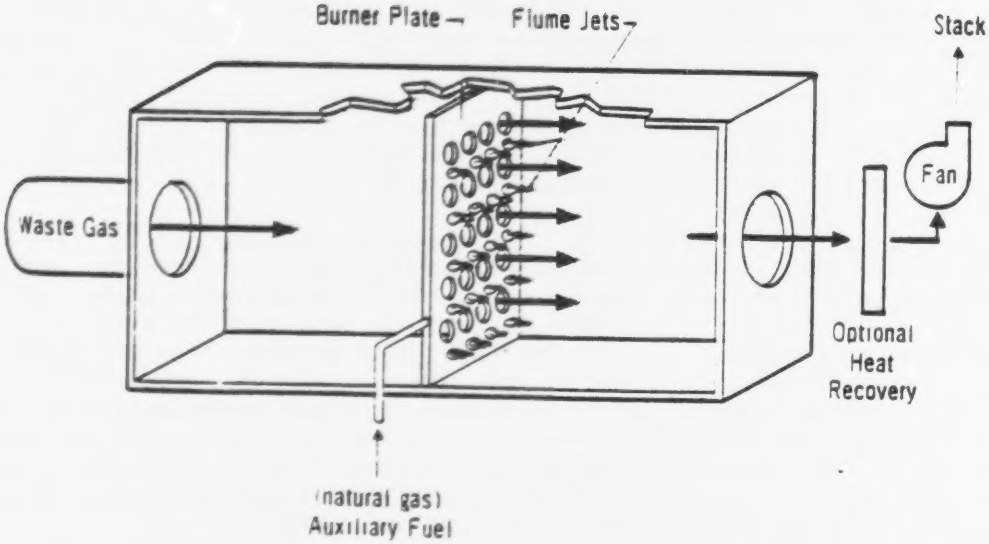
Burner Plate
Flume Jets
Stack
Fan
Waste Gas
Optional Heat Recovery
(natural gas) Auxiliary Fuel

Figure 3–6. Distributed burner, thermal oxidizer.

3.5.3.3 Thermal Oxidizer Emission Destruction Effectiveness. Based on a study of thermal oxidizer efficiency, cost and fuel use, it is concluded that 98 percent VOC reduction, or 20 ppmv as compound exit concentration (whichever is less stringent) is the highest reasonable control level achievable by all new incinerators in all air oxidation processes, considering current technology.[40] An analysis assuming achievement of this efficiency with incinerator operation at 870°C (1600°F) and 0.75 second residence time yields conservative estimates of costs and energy use.

The VOC destruction efficiency of an incinerator can be affected by variations in chamber temperature, residence time, inlet concentration, compound type, and flow regime (mixing). A combustion chamber temperature of 870°C (1600°F) was chosen for the analysis on the basis that higher temperatures, with higher control efficiencies, are preferred. Test results show that 98 percent destruction efficiency is achievable at various temperatures (700°C (1300°F) to 800°C (1500°F)) and residence times (0.5 to 1.5 seconds).[41] Kinetics calculations comparing the test conditions to 870°C (1600°F) temperature with 0.75 second residence time show that the latter set of conditions is more conducive to complete VOC destruction. Cost per pound of VOC controlled increases only 5 to 10 percent with an increase in temperature from 760°C (1400°F) to 870°C (1600°F) with the use of 70 percent recuperative heat recovery. Temperature higher than 870°C (1600°F) are not desirable due to the materials limitations of metallic heat exchangers. Higher temperatures would require heat exchange surfaces to be made of more expensive materials.

Variations in inlet concentration can change a thermal oxidizer's VOC destruction efficiency. Kinetics calculations describing the complex combustion reaction mechanisms point to much slower reaction rates at very low compound concentrations. Available data show that 20 ppmv as compound minimum outlet concentration is a reasonable limit which allows for the drop in achievable destruction efficiency with decreasing inlet concentration.[42]

The data also show that the impact of compound variation on destruction efficiency increases at temperatures lower than 760°C (1400°F), although precise quantitative relations could not be determined. The types of compounds in the data include C_1 to C_5 alkanes and olefins, aromatics such as benzene, toluene, and xylene and oxygenated compounds such as MEK and isopropanol. Nitrogen-containing species such as acrylonitrile and ethylamines and chlorinated compounds such as vinyl chloride are also included in the data.

At temperatures over 760°C (1400°F), the oxidation reaction rate is much faster than the rate at which mixing takes place. Therefore, VOC destruction becomes more dependent upon the fluid mechanics within the oxidation chamber. The flow regime should be such that the mixing of the VOC stream, combustion air, and hot combustion products from the burner be rapid and thorough. This enables the VOC to attain the combustion temperature in the presence of enough oxygen for a sufficient period of time for the oxidation reaction to reach completion. Chamber design and burner and baffle configurations provide for turbulent flow for improved mixing. The most practical manner of achieving good mixing and efficiency is to adjust the installed equipment to improve performance.

3.5.4 Catalytic Oxidizers

Catalytic oxidation is the second major combustion technique for VOC emissions control. Selected air oxidation processes known to use catalytic oxidation for emission control are listed in Table 3-6.

A catalyst works by changing the rate of a chemical reaction without becoming permanently altered itself. Catalysts for catalytic oxidation cause a higher rate of reaction at a lower energy level (temperature), allowing oxidation of VOC at lower temperatures than for thermal oxidation. Combustion catalysts include platinum and platinum alloys, copper oxide, chromium and cobalt.[43] These are deposited in thin layers on inert substrates to provide for maximum surface contact area.

3.5.4.1 Catalytic Oxidation Process. In catalytic oxidation, a waste stream and air are contacted with a catalyst at a temperature sufficiently high to allow the oxidation reaction to occur. The waste gas is introduced into a mixing chamber where it is heated to the proper temperature (about 316°C (600°F)) by contact with the hot combustion products of a burner. The heated mixture is then passed through the catalyst bed as shown in Figure 3-7. VOC and oxygen are transferred to the catalyst surface by diffusion from the waste gas and chemisorbed in the pores of the catalyst to the active sites where the oxidation reaction takes place. The reaction products are then desorbed from the active sites and transferred by diffusion back into the waste gas.[44] The cleaned gas may then be passed through a waste heat recovery device before exhausting into the atmosphere.

3.5.4.2 Catalytic Oxidizer Emission Reduction Effectiveness. Catalytic oxidizers operating at 450°C (840°F) are able to oxidize waste gases as effectively as thermal oxidizers operating at 750°C (1380°F).[45] Catalytic oxidizer VOC destruction efficiencies of 95 percent have been reported in various cases and efficiencies of 97.9 to 98.5 percent are attainable in some systems.[46]

3.5.4.3 Parameters Affecting VOC Destruction Efficiency. Catalytic oxidizer destruction efficiency is dependent on catalyst volume per unit volume gas processed, operating temperature, and waste gas VOC composition and concentration. A typical catalyst bed contains about 0.014 to 0.057 m^3 of catalyst bed volume (0.5 to 2.0 ft^3) for each 28 Nm^3 m (1000 scfm) of waste gas flow.[47] Greater efficiencies can be attained by an increase in the volume ratio; however, the cost of a larger catalyst bed can become prohibitive.

The operating temperature range of combustion catalysts is usually from 316°C (600°F) to 650°C (1200°F). Lower temperatures may result in slowing down and possibly stopping the oxidation reaction. Higher temperatures may result in shortened catalyst life and possible evaporation of the catalyst from the support substrate.

Accumulation of particulate matter or condensed polymerized material can block the active sites and reduce effectiveness. Catalysts can also be deactivated by compounds containing sulphur, bismuth, phosphorous, arsenic, antimony, mercury, lead, zinc, or tin.[48]

TABLE 3-6. SELECTED AIR OXIDATION PROCESSES KNOWN TO USE CATALYTIC OXIDATION FOR EMISSION CONTROL

Chemical
Acrylonitrile
Ethylene Dichloride
Ethylene Oxide
Maleic Anhydride

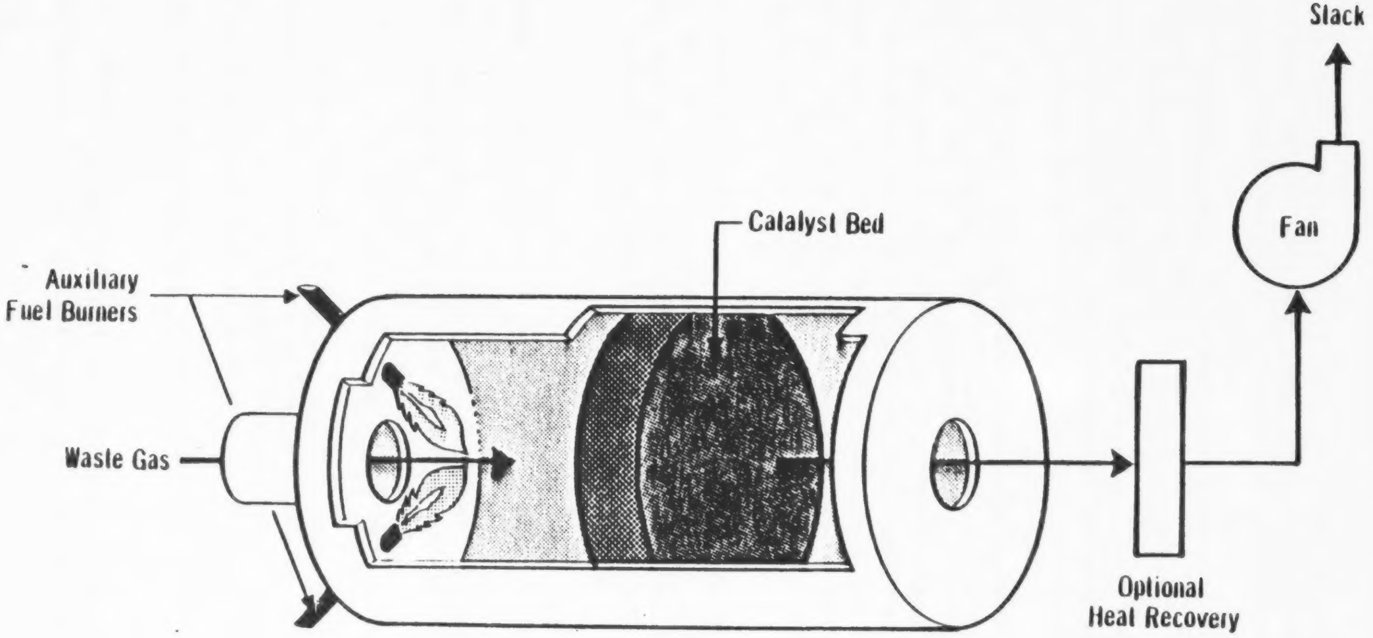
Stack
Fan
Catalyst Bed
Auxiliary Fuel Burners
Waste Gas
Optional Heat Recovery

Figure 3–7. Catalytic oxidizer.

Conditions such as those noted above can result in VOC passing through or incomplete oxidation with the formation of aldehydes, ketones, and organic acids.

Sensitivity to waste stream flow condition variations and inability to handle moderate heating value streams limit the application of catalytic oxidizers as SOCMI air oxidation process vent emission controls.

3.5.5 Advantages and Disadvantages of Control by Combustion

VOC control by combustion has several advantages: (1) a properly designed and operated combustion device can provide destruction of nearly all VOC; (2) most combustion units are capable of adapting to moderate changes in effluent flowrate and concentrations; and (3) control efficiency is insensitive to the specific VOC pollutant relative to product recovery techniques.

There are also disadvantages associated with VOC control by combustion: (1) high capital and operating costs result from thermal oxidation techniques, which could require a plot of land as large as 300 ft by 300 ft for installation; (2) since offgas must be collected and ducted to the afterburner, long duct runs may lead to condensation of combustibles and possibly to duct fires; and (3) since thermal oxidizers utilize combustion with a flame for achieving VOC destruction, the unit must be located at a safe distance from process equipment in which flammable chemicals are used. Alternatively, special designs may be employed to minimize the risk of explosion or fire.

There are several disadvantages particularly associated with control of halogenated VOC by combustion: (1) halogen acids produced by the combustion must be removed by flue gas scrubbing; (2) water and caustic are required at the site for scrubbing the flue gas; and (3) proper waste disposal of the salt formed during flue gas scrubbing is required.

3.6 STATE REGULATIONS FOR VOC CONTROL

Over 90 percent of the total SOCMI production capacity is located in 14 states, with over half of that percentage being in Texas and Louisiana. Of the 14 states only Texas, Louisiana, New Jersey, and Illinois have VOC emission regulations applicable to SOCMI air oxidation processes.[49]

1. Texas facilities emitting more than 100 lbs/day and at an instantaneous rate greater than 250 lbs/hr are required to "properly" incinerate waste gases at 704°C (1300°F).
2. Louisiana requires incineration at 704°C (1300°F) with 0.3 seconds residence time or control by other acceptable methods. The regulations can be waived if the offgas will not support combustion.
3. New Jersey has based its SIP's on a sliding scale with allowable emission rate based on difficulty of control.
4. Illinois limits all VOC emissions to 100 ppm equivalent methane (CH_4).

3.7 TECHNICAL FEASIBILITY OF RETROFITTING CONTROL DEVICES[50-56]

The difficulties encountered in retrofitting control devices are similar.

Retrofit construction can involve demolition, crowded construction working conditions, scheduling construction activities with production activities, and longer interconnecting piping. Utility distribution systems and load capacities may not be adequate to accommodate the control equipment, and extra circuit breakers may be required.

Retrofitted control devices are preferably located on the ground near the process vents, but can be raised on platforms or mounted on the roof in order to accommodate other processes. There must be sufficient room around the units to allow for maintenance, and the exhausts must not present a hazard to equipment or personnel. Each requires electricity to operate fans, control and recording equipment. Valves and dampers may be pneumatically operated, requiring compressed air lines. Adsorption devices may also need steam for regeneration. Condensers probably need a refrigeration plant and coolant lines.

Retrofits may require remodeling of existing structures and coordination of the construction efforts with process operations.

Since thermal oxidizer systems require a relatively large land area and the safety aspects of an open flame are an important factor, the longer interconnecting piping probably is the most significant retrofit factor. Because offgas containing halogenated VOC requires combustion temperatures above those for which recuperative heat recovery is feasible, a waste heat boiler must be used for heat recovery. Since it may be costly for some companies to have excess steam on-site, it may not be practical for all companies to utilize the heat recovery option. In a retrofit situation, it may be difficult to locate the waste heat boiler close to the steam-consuming site.

Data on retrofit requirements and costs for thermal oxidizers, recuperative heat exchangers, and waste heat boilers are given in Reference 56.

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4. ENVIRONMENTAL ANALYSIS OF REASONABLY AVAILABLE CONTROL TECHNOLOGY (RACT)

This chapter discusses the nature and environmental impact of reasonably available control technology (RACT) for SOCMI air oxidation process reactors and associated product recovery vents. The environmental analysis considers both the effects attributed directly to the application of RACT, such as reduced VOC emissions, and those that are indirect or induced, such as aggravation of other pollutant problems. The beneficial and adverse effects on air quality, water quality, solid waste disposal, and energy use are analyzed.

4.1 RACT RECOMMENDATION

The recommended RACT (hereafter referred to as RACT) would be applicable to air oxidation facilities within the SOCMI. This would include all reactors in which air is used as an oxidizing agent to produce an organic chemical. The air oxidation facility to which RACT would apply is a product recovery system and all associated reactors discharging directly into that system, or any reactor(s) discharging directly to the atmosphere. The product recovery system refers to any equipment used to collect VOC for beneficial use or reuse, such as for sale or recycling. Some examples of product recovery systems are absorbers, adsorbers, and condensers as well as certain devices that recover non-VOC's (such as ammonia and HCl recovery units). The RACT would require, for each air oxidation process vent stream, either use of a combustion device which reduces total organic compound emissions (minus methane and ethane) by 98 weight percent or to 20 ppm by volume (ppmv), whichever is less stringent, or maintenance of a total resource effectiveness (TRE) index value greater than 1.0. The meaning of RACT is explained more fully in the following paragraphs.

Experience indicates that many types of control devices can be used to reduce air oxidation process VOC emissions. However, thermal oxidation is the only demonstrated VOC control technology universally applicable to all SOCMI air oxidation processes. All new incinerators can achieve at least a 98 weight percent VOC reduction or 20 ppmv exit concentration (whichever is less stringent). Although projection of the RACT impacts is based on the use of thermal oxidation, the RACT itself would not specify thermal oxidation as the only VOC control method. Other control devices such as flares, boilers, process heaters, and catalytic oxidizers have been demonstrated to achieve 98 percent destruction efficiency where applicable. The RACT would permit the use of alternate devices as long as the 98 percent destruction or 20 ppmv emissions limits are met. It is recommended that air oxidation facilities for which an existing combustion device is employed to control process VOC emissions should not be required to meet the 98 percent emissions limit until the combustion device is replaced for other reasons. In other words, no facility would be required to upgrade or replace an existing combustion device.

The RACT is based on incineration of certain process vent streams discharged to the atmosphere. The streams for which RACT involves this VOC reduction are those for which the associated total resource-effectiveness

(TRE) index value is less than 1.0. An index value of TRE can be associated with each air oxidation vent stream for which the offgas characteristics of flowrate, hourly VOC emissions, corrosion properties, and net heating value are known. For facilities having a TRE index value which exceeds the cutoff level, a VOC emissions reduction of 98 percent or to 20 ppmv would not be required under the recommended RACT.

The TRE index is a measure of the supplemental total resource requirement per unit VOC reduction, associated with VOC control by thermal oxidation. All resources which are expected to be used in VOC control by thermal oxidation are taken into account in the TRE index. The primary resources used are supplemental natural gas, capital, and (for offgas containing halogenated compounds) caustic. Other resources used include labor, electricity, and (for offgas containing halogenated compounds) scrubbing and quench makeup water. TRE is further defined and discussed in Chapter 5 and Appendix D.

The TRE index is a convenient, dimensionless measure of the total resource burden associated with VOC control at a facility. Overall, the TRE index is independent of the general inflation rate insofar as it assumes fixed relative costs of the various resources, such as carbon steel and electricity. However, the TRE index accounts for the fact that natural gas costs are rising at a rate higher than the general inflation rate. The natural gas cost used in the index was derived by taking the natural gas price projected for the year 1990 weighted geographically. This 1990 gas price was then deflated to 1980 dollars. The weighting scheme was derived by taking individual gas price projections for the year 1990 for each of the 10 EPA regions. These projections were weighted according to the percentage of total air oxidation plant capacity within each region. The 1990 natural gas price used in the TRE index reflects the summation of the values for each region.

The TRE index cutoff level associated with the RACT recommendation has the value 1.0. Those facilities with a process vent stream or combination of process vent streams having a TRE index value below 1.0 would reduce VOC emissions by 98 percent under RACT. An equation for the calculation of the TRE value of an individual facility as a function of the offgas flowrate, hourly VOC emissions, corrosion properties, and heating value is derived and presented in Appendix D.

The distinction in RACT, between facilities with a TRE index value above the cutoff level of 1.0 and those with a value below it, encourages the use of product recovery techniques or process modifications to reduce emissions. As discussed in Appendix D, the values of offgas flowrate, hourly VOC emissions, corrosion properties, and net heating value are used to calculate the TRE value of a given facility. These values are measured and/or determined for the vent stream at the outlet of the final product recovery device. Use of additional product recovery is expected to decrease VOC emissions and increase the total resource-effectiveness associated with thermal incineration of a vent stream.

It is intended for RACT to cover air oxidation facilities that emit VOC (i.e., compounds which participate in atmospheric photochemical reactions to produce ozone.) Since compounds with negligible photochemical reactivity do not participate in the production of ozone, it is recommended that they be excluded when determining a TRE index. Therefore, in determining hourly emissions rate for input into the TRE equation, a facility should measure total organic compounds and subtract those compounds which have been identified to have negligible photochemical reactivity. Those compounds which the Administrator has concluded have a negligible photochemical reactivity are identified in EPA statements on ozone abatement policy for SIP revisions (42 FR 35314; 44 FR 32042; 45 FR 32424; 45 FR 4894).

The environmental analysis used a national statistical profile, representing the air oxidation segment of SOCMI, to estimate the cost and energy impacts of RACT. Appendix B describes the statistical profile and the specific method of projecting the RACT impacts.

4.2 AIR POLLUTION

The principal impact of RACT on air pollution would be beneficial and would consist of a reduction in national VOC emissions. The hourly and annual quantities of VOC released overall, before and after control by RACT, are presented in Table 4-1. The overall emissions represent the total amount of VOC released from the 47 air oxidation plants in ozone nonattainment areas requesting extension. Table 4-2 shows hourly and annual VOC emissions, before and after control by RACT, from an average air oxidation plant. The average plant emissions represent the amount of VOC released from one of the estimated 14 air oxidation plants that would control VOC under RACT. However, because of the diversity of air oxidation vent streams, actual VOC emissions differ at individual facilities. Under current control levels, the national VOC emissions from the affected air oxidation facilities are 40,390 Mg/yr (44,430 tons/yr). The application of RACT would reduce these emissions by 53 percent to 19,015 Mg/yr (20,915 tons/yr).

Pollutants generated by the combustion process, particularly nitrogen oxides (NO_x), have the potential to affect the ambient air quality. The principal factors affecting the rate of NO_x formation are the amount of excess air available, the peak flame temperature, the period of time that the combustion gases are at peak temperature, and the rate of cooling of the combustion products.[1] Because of the relatively low combustion temperatures and relatively short residence times associated with control of VOC using thermal oxidation, the rate of NO_x formation is expected to be low.

Thermal oxidizer outlet concentrations of NO_x were measured in seven sets of thermal oxidizer tests conducted at three air oxidation plants. The test results indicate that NO_x outlet concentrations range from 8 to 200 ppmv (0.015 to 0.37 g/m^3). These values could increase by several orders of magnitude in a poorly-designed or operated unit. The tests are described and documented in Appendix A.

Although there are conflicting data, some studies report that incineration of vent streams containing high levels of nitrogen-containing compounds may cause increases in NO_x emissions.[2] The maximum outlet NO_x concentration of 200 ppmv was measured at an acrylonitrile plant. The vent stream of this plant does contain nitrogenous compounds. The NO_x outlet concentrations measured at the other two plants, whose vent streams do not contain nitrogenous compounds, range from 8 to 30 ppm (0.015 to 0.056 g/m^3).

TABLE 4-1. ESTIMATED VOC EMISSIONS FROM PROCESS VENTS OF AIR OXIDATION FACILITIES IN OZONE NONATTAINMENT AREAS

	VOC Emissions at Uncontrolled Levels		VOC Emissions at Current SIP Levels[b]		VOC Emissions After Control by RACT	
	kg/hr	Mg/yr	kg/hr	Mg/yr	kg/hr	Mg/yr
Air oxidation process vent emissions from estimated 14 facilities required to control VOC	5,920	51,860	2,490	21,810	50	435[c]
Air oxidation process vent emissions from estimated 33 facilities not required to control VOC	5,050	44,240	2,120	18,580	2,120	18,580
Estimated overall emissions[a]	10,970	96,100	4,610	40,390	2,170	19,015[d]

[a] Overall emissions represent the amount of VOC released from the process vents of 47 air oxidation facilities in ozone nonattainment areas requesting extension.

[b] Equivalent to 58 percent VOC reduction from uncontrolled levels. The 58 percent value for baseline control is presented in Appendix B.

[c] Equivalent to 98 percent reduction from current SIP levels.

[d] Equivalent to 53 percent VOC reduction from current SIP levels.

TABLE 4-2. ESTIMATED VOC EMISSIONS FROM PROCESS VENTS FOR AN AVERAGE AIR OXIDATION FACILITY

	VOC Emissions at Uncontrolled Levels		VOC Emissions at Current SIP Levels[a]		VOC Emissions After Control by RACT	
	kg/hr	Mg/yr	kg/hr	Mg/yr	kg/hr	Mg/yr
Average plant emissions (for estimated 14 facilities required to control VOC)[c]	423	3,705	178	1,560	3.56	31.2[b]
Average plant emissions (for estimated 33 facilities not required to control VOC)[d]	153	1,340	64	560	64	560

[a] Equivalent to 58 percent VOC reduction from uncontrolled levels. The 58 percent value for baseline control is presented in Chapter 2.

[b] Equivalent to 98 percent VOC reduction from current SIP levels.

[c] Average amount of VOC released (assuming 77 percent capacity utilization) from the process vent of one of the estimated 14 air oxidation plants that would be estimated to control VOC under RACT. Because of the diversity of air oxidation vent streams, actual VOC emissions will differ at individual plants.

[d] Average amount of VOC released (assuming 77 percent capacity utilization) from the process vent of one of the estimated 33 air oxidation plants that would not be estimated to control VOC under RACT. Because of the diversity of the air oxidation vent streams, actual VOC emissions will differ at individual plants.

Control of VOC emissions from oxychlorination vent streams by thermal oxidation may result in the release of chlorinated combustion products to the environment. Flue gas scrubbing can be used to remove these compounds from the incinerator outlet stream. However, incineration temperatures greater than 871°C (1600°F) are required for destruction of halogenated VOC. At temperatures of 980° to 1205°C (1800° to 2200°F), almost all chlorine present exists in the form of hydrogen chloride (HCl), a form easily removed by scrubbing. The HCl emissions generated by thermal oxidation at these temperatures can be removed efficiently by scrubbing with water. The equation used to determine the TRE index for a halogenated vent stream includes the costs associated with using such a scrubber.[3,4]

4.3 WATER POLLUTION

The impact of RACT on water pollution is minimal. Control of VOC emissions using thermal oxidation does not result in any significant increase in wastewater discharge by air oxidation unit processes. Small quantities of hazardous waste are generated as a result of thermal oxidizer operation. Such waste would be covered under the Resource Conservation and Recovery Act (RCRA).

Use of an incinerator/scrubber system for control of VOC emissions from oxychlorination vent streams results in increased water consumption. In this type of control system, water is used to remove the HCl contained in the thermal oxidizer outlet stream. The increase in total plant wastewater would be relatively small and would not overload plant waste treatment or sewer capacity. However, the absorbed HCl may cause the water leaving the scrubber to have a low pH. This acidic effluent could lower the pH of the total plant effluent if it is released into the plant wastewater system.

The water effluent guidelines for individual States may require that industrial sources maintain the pH of water effluent within specified limits. To meet these guidelines, the water used as a scrubbing agent must be neutralized prior to discharge to the plant effluent system. The scrubber effluent can be neutralized by adding sodium hydroxide (NaOH) to the scrubbing water. The amount of NaOH needed depends on the amount of HCl in the incinerator outlet stream. Approximately 1.09 kg (2.4 lb) of NaOH are needed to neutralize 1 kg (2.2 lb) of HCl. The salt formed must be purged from the system and properly disposed of. Acceptable methods of disposal include direct waste water discharge or recovery of the NaCl.[5]

The increased water consumption and NaOH costs were included in the projected operating costs for those facilities with halogenated vent streams. Costs associated with disposal of NaCl were judged to be insignificant because all facilities can directly discharge the brine at little or no cost into the ocean, a brackish stream, or a sewer system. The makeup rate for water purged from the system, based on one percent dissolved solids in the water recycle, is 0.333 m^3/kg (19.2 gal/lb) of chlorine in the waste gas.

The use of scrubbers to remove HCl from the incinerator offgas also could result in small increases in the quantities of organic compounds, such as 1,2-dichloroethane, released into plant wastewater. Organic compound emissions into the water and, subsequently, into the air, can be prevented by using a water stripper.

4.4 SOLID WASTE DISPOSAL

There are no significant solid wastes generated or disposed of as a result of control by RACT. A small amount of solid waste disposal would result if catalytic oxidation were used by a facility, instead of thermal oxidation, to achieve an equivalent degree of VOC control. The solid waste would consist of spent catalyst. If a facility were to use an additional absorption column for improved product recovery in order to become exempt from a VOC reduction requirement, a small amount of solid waste would be generated by cleaning the column.

4.5 ENERGY

The energy impacts of control by RACT are based on using thermal oxidation to control VOC emissions. Maintenance of the required thermal oxidizer operating conditions requires supplemental fuel, commonly in the form of natural gas. The amount of supplemental fuel needed depends on offgas temperature, flow and heating value, incineration temperature, and type of heat recovery used. Due to the use of heat recovery techniques, combustion of some air oxidation vent streams results in a net production of energy even though supplemental fuel is necessary for flame stability. Up to 70 percent heat recovery can be achieved at any facility by using techniques currently employed in the air oxidation industry.

In addition to supplemental fuel, electricity requirements contribute to the total energy use for VOC control. Electricity is required to operate equipment such as the pumps, fans, blowers, and instrumentation that may be necessary to control VOC using a thermal oxidizer or a thermal oxidizer/ scrubber system. Total electrical needs are relatively small compared to energy requirements in the form of supplemental fuel for thermal oxidation.

The total additional national energy requirements after application of RACT are estimated to be 5,000 TJ/yr (4.89×10^{12} Btu/yr). The overall energy requirements represent the total amount of supplemental fuel, in the form of natural gas, estimated to be used by the 14 air oxidation facilities that would control VOC emissions under RACT.

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5. CONTROL COST ANALYSIS OF RACT

5.1 INTRODUCTION

The costs of implementing RACT for control of volatile organic compound (VOC) emissions from SOCMI air oxidation process vents are presented in this chapter. Capital costs, annualized costs, and the cost-effectiveness of RACT are presented.

5.1.1 Substitution of National Profile for Model Plant

The RACT cost impacts were estimated based on natural gas-fired thermal oxidation as the single control technique. For offgas that contains halogenated compounds, a design temperature of 1100°C (2000°F) and a residence time of 1.0 second were used. For offgas lacking halogenated compounds, a design temperature of 870°C (1600°F) and residence time of 0.75 second were used. These design parameters represent the worst-case conditions under which a VOC destruction efficiency of 98 percent would be attained.

The RACT impacts were not based on the traditional model plant approach. Because of the number and diversity of facilities and manufacturing processes in the air oxidation industry, a large number of model plants would have been required in order to accurately determine the cost impacts associated with RACT. However, only a limited amount of waste stream data is required to determine incinerator costs and efficiency. The required data include offgas flowrate, net heating value, and VOC emission rate. It must also be known whether the offgas contains halogenated compounds. Therefore, although data from many types of processes are still required in order to adequately represent the air oxidation industry, the data need not consist of fully designed model plants. Rather, a national statistical profile of air oxidation processes was constructed. The national profile characterizes air oxidation processes according to national distributions of the three critical offgas parameters for halogenated and nonhalogenated waste streams. The RACT cost impacts are therefore evaluated as impacts upon the entire population of affected facilities, as represented by the national profile. The development and statistical basis for the national profile are described in detail in Appendix B.

5.1.2 Thermal Oxidation Design Categories[1-7]

The thermal oxidizer system design employed for a particular vent stream depends upon the offgas net heating value, the flowrate, and the presence or absence of halogenated compounds. Sufficient fuel must be added to permit incineration at 870°C (1600°F). Fuel requirements can be reduced by the use of recuperative heat recovery to preheat the offgas and/or combustion air. Secondary heat recovery in addition to the heat exchanger is, in general, neither technically nor economically feasible. The basic design characteristics of each category are given in Table 5-1.

5.1.2.1 Categories A1 and A2. All vent streams which contain halogenated compounds are included in Categories A1 and A2. Due to the greater difficulty of achieving complete combustion of chlorinated VOC, an incineration temperature of 1100°C (2000°F) and a one second residence time

TABLE 5-1. BASIC CHARACTERISTICS OF EACH DESIGN CATEGORY[1-7]

Category	Minimum Net Heating Value (MJ/scm)	Maximum Net Heating Value (MJ/scm)	Incineration Temperature C	Residence Time (Sec)	Type of Heat Recovery	Stream(s) Preheated	Percent Heat Recovery	Additional Control Equipment
A1[a]	0	3.5	1100	1.0	Waste-Heat Boiler	None	60%	Flue Gas Scrubber
A2[a]	3.5	-	1100	1.0	Waste-Heat Boiler	None	60%	Flue Gas Scrubber
B	0	0.48	870	0.75	Recuperative Heat Exchanger	Offgas and Combustion Air	70%	None
C	0.48	1.9	870	0.75	Recuperative Exchanger	Combustion Air Only	34%	None
D	1.9	3.6	980	0.75	None	None	-	None
E	3.6	-	980	0.75	None	None	-	None

[a] Offgas contains halogenated compounds.

were assumed. Combustion temperatures exceeding 870°C (1600°F) rule out the use of recuperative heat exchangers because of problems with materials of construction and with associated problems such as possible precombustion occurring in the exchangers. However, a waste heat boiler can be used effectively with temperatures up to and above 1650°C (3000°F). The only air oxidation process which has chlorinated offgas is ethylene dichloride manufacture, which is known to employ waste heat boilers for heat recovery. Therefore, heat recovery in a waste heat boiler with steam generation was assumed. The amount of heat recovery was limited by a minimum outlet flue gas temperature of about 260°C (500°F), below which, excessive condensation of corrosive combustion products could occur.[8] The corrosive hydrogen chloride is then removed by flue gas quenching and scrubbing, and the resulting solution neutralized with caustic soda. Categories A1 and A2 do not differ in control system design, but only in supplementary fuel requirements.

5.1.2.2 Category B. Design Category B includes offgas with a heating value below 0.48 MJ/scm (13 Btu/scf), which corresponds to 25 percent of a typical lower explosive limit (LEL) in air.[9] For Category B, 70 percent heat recovery was assumed. In this heating value range, the amount of heat recovery which could be used is only limited by a ceiling of about 550-600°C (1000-1100°F) on the combustion air preheat temperature due to burner design considerations.[10]

5.1.2.3 Category C. Because of insurance requirements, offgas with a heating value between 0.48 MJ/scm (13 Btu/scf) and 1.9 MJ/scm (52 Btu/scf), which constitutes Category C, may not be preheated.[11] This heating value range corresponds to a range of 25-100 percent of LEL in air for a typical organic vapor. Because air oxidation vent streams generally contain little or no oxygen, which is essentially depleted by the process reaction, offgas in this heating value range need not be diluted.[12] It was assumed that the combustion air would be preheated, with 34 percent of the flue gas heat content recovered.[13]

5.1.2.4 Category D. Offgas with a heating value in the range 1.9 MJ/scm (52 Btu/scf) to 3.6 MJ/scm (98 Btu/scf), which constitutes Category D, need not be preheated and requires only a small amount of auxiliary fuel, for flame stability. The offgas determines its own combustion temperature, which in general, exceeds 870°C (1600°F) and can be as high as 980°C (1800°F). A design temperature of 980°C (1800°F) was assumed, because of the larger chamber volume per mole of offgas and greater amount of refractory required at that temperature.

5.1.2.5 Category E. Design Category E includes offgas with a heating value above 3.6 MJ/scm (98 Btu/scf). Offgas in Category E need not be preheated and requires only a small amount of auxiliary fuel, for flame stability. The offgas, which determines its own combustion temperature, will burn at temperatures of 980°C (1800°F) or greater. Some processes and facilities with offgas this rich are able to use the steam which would be generated by employing a waste heat boiler after the thermal incinerator or by combusting VOC in an existing boiler or process heater. Other facilities, however, will not be able to use steam and will not employ heat recovery. A few facilities might choose to dilute the offgas so that the flue gas temperature does not exceed 980°C (1800°F). In order to give a conservative estimate of costs, it was assumed that streams in Category E were diluted to 3.6 MJ/scm (98 Btu/scf), and that no heat recovery was employed.

5.1.2.6 Maximum Equipment Sizes. Because of shipping size restrictions, single thermal oxidizer units larger than about 32 feet by 16 feet would require field fabrication, which would greatly increase the cost.[14] Therefore, it is assumed that vent streams which would require larger incinerators would instead employ multiple sets of control equipment systems. The design standard temperature vent stream (incinerator inlet) flowrates, for each design category, which correspond to the maximum equipment size are given in Table 5-2.[15,16]

5.1.3 Offgas Composition Assumptions

Facilities with a flowrate less than 500 scfm are assumed to have a flowrate of 500 scfm for the purpose of calculating capital costs. In order to avoid underestimation of the required equipment sizes, all vent streams were assumed to contain no oxygen. Therefore, combustion air requirements were maximal. In order to increase the rate of combustion and avoid incomplete combustion and pyrolysis, it was assumed that enough excess combustion air was supplied to assure three mole percent oxygen in the flue gas.[17]

An average VOC molecular weight was calculated for the national profile.[18] Based on additional calculations by Enviroscience, all nonhalogenated VOC were assumed to consist of a typical model compound with the empirical formula $C_{2.8}H_{5.7}O_{0.63}$.[19] All halogenated VOC were assumed to consist of a typical compound with the empirical formula $C_{1.4}H_{2.4}Cl_{0.86}$.[20] Based on an inspection of the national profile, it was further assumed that each stream contained four moles of methane per mole of VOC. From these offgas compositions, a typical ratio of flue gas flow to offgas flow was calculated for each design category and used to size the control equipment. These ratios are given in Table 5-3.[21,22] An offgas temperature of 38°C (100°F) was assumed.[23] The model nonhalogenated VOC were assumed to have a net heating value of 76 MJ/scm, while a net heating value of 29 MJ/scm was assumed for the model halogenated VOC. These values correspond to net heating values of acetone and methyl chloride, respectively.[24,25] These offgas composition assumptions were also used to determine the minimum and maximum net heating values for each design category. However, actual vent stream parameters were used in all other parts of the analysis. Actual offgas parameters were used in calculations for typical vent streams in each design category, RACT impacts, and total resource-effectiveness projections.

5.2 BASIS FOR CAPITAL COSTS

The capital costs for the implementation of RACT include purchase costs and retrofit installation costs for thermal incinerators, recuperative heat

TABLE 5-2. MAXIMUM OFFGAS FLOWRATES EACH DESIGN CATEGORY[15,16]

Category	Incineration Temperature (°C)	Residence Time (Sec)	Maximum Design Vent Stream (Incinerator Inlet) Flowrate (Thousand scm/min)
A1	1100	1.0	0.74
A2	1100	1.0	0.74
B	870	0.75	1.42
C	870	0.75	1.42
D	980	0.75	1.25
E	980	0.75	1.25

TABLE 5-3. RATIO OF FLUE GAS FLOWRATE TO OFFGAS FLOWRATE FOR EACH DESIGN CATEGORY[21,22]

Category	Maximum Net Heating Value (MJ/scm)	Incineration Temperature (°C)	Ratio of Flue Gas Flow to Offgas Flow[a]
A1[b]	3.5	1100	2.9
A2[b]	-	1100	2.9
B	0.48	870	1.9
C	1.9	870	2.3
D	3.6	980	2.5
E	-	980	2.5

[a] Both at standard temperature.

[b] Offgas contains halogenated compounds.

exchangers, ducts, fans, and stacks and supporting structures for the ductwork. For halogenated streams, the purchase and retrofit installation costs of waste heat boilers and flue gas scrubbers are also included.

The basic capital cost data were provided by the IT Enviroscience thermal oxidizer evaluation documents and were derived from vendor quotations.[26,27] The IT Enviroscience documents were specifically designed for air oxidation processes, which have vent streams containing little or no oxygen. Therefore, they take into account the maximum combustion air requirements for incineration of such streams. Furthermore, the Enviroscience documents present costs for a range of offgas heating values and incineration temperatures. Total installed costs are presented for two types and several levels of heat recovery. It was necessary to use a cost source possessing this flexibility to cover the variety of air oxidation vent stream characteristics. The Enviroscience costs were based on December 1979. In order to transform these to June 1980 costs, an escalation factor of 1.056 was used. This factor is the ratio of the Chemical Engineering M&S chemical industry equipment cost index value for the second quarter, 1980, to that for the fourth quarter, 1979.[28]

The relation of the Enviroscience purchase cost estimates to the original vendor quotations is discussed in Appendix E. Graphs relating purchase costs to offgas flowrates are also given in Appendix E for each piece of control equipment. As discussed in that appendix, purchase cost estimates obtained from two additional vendors agreed well with the Enviroscience estimates.

Enviroscience estimates equipment installed costs from equipment purchase costs by adding factors for each of 10 aspects of installation. These factors are expressed as percentages of the equipment purchase cost. Enviroscience also estimates an overall control system installed cost for each design category. Because the Enviroscience installation factors are for new sources, EPA used this method and some additional data to estimate a set of retrofit installation factors.[29] The most important factors are those for piping and erection. A list of the installation components for which factors were developed is given in Table 5-4.[30] A detailed discussion of the derivation and use of the installation factors is given in Appendix E. In order to reflect the retrofit installation costs, a retrofit correction factor of 1.625, derived in Appendix E as the ratio of retrofit to new source installation factors, was employed. This factor was multiplied by the new source overall installed cost estimated for each control system by Enviroscience.

The total installed capital costs represent the total investment, including all indirect costs such as engineering and contractors' fees and overhead, required for purchase and installation of all equipment and material to provide a facility as described. These are battery-limit costs and do not include the provisions for bringing utilities, services, or roads to the site, the backup facilities, the land, the research and development required, or the process piping and instrumentation interconnections that may be required within the process generating the waste gas feed to the thermal oxidizer.[31]

TABLE 5-4. INSTALLATION COMPONENTS

Installation Component
Foundation
Insulation
Structures
Erection
Piping
Painting
Instruments
Electrical
Fire Protection
Engineering, Freight and Taxes

The basis for the capital costs is further discussed below for each design category. Total installed capital cost equations as a function of operating offgas flowrate were developed and are described in Table 5-5 for each design category.

It was assumed that at typical operating offgas flowrate would be 95 percent of the design maximum. Therefore, a design vent size factor of 0.95 was assumed to avoid an underestimate of control equipment size and capital cost. These capital cost equations were obtained by fitting an analytical function of capital cost versus design offgas flowrate to the data in the Enviroscience tables and graphs. A different cost curve was fitted for each design category.

All three coefficients were estimated for the Category B equation. The exponent was estimated to be 0.88. This exponent was assumed for the other design categories, and only the remaining two coefficients were fitted for them. These equations are judged to be reasonably close fits, and no claim is made that they are the best ones that could have been statistically determined. Capital cost estimates for a hypothetical vent stream with characteristics which are average for each design category are presented in Table 5-6. It was estimated that retrofit total installed costs would approximately equal the product of the retrofit correction factor of 1.625 multiplied by the new source total installed cost of a control system as estimated by Enviroscience, escalated to June 1980 dollars.

5.2.1 Common Control Equipment

Several pieces of control equipment are common to each design category. These include the thermal oxidizer, ductwork and supports, fans, and stack.

5.2.1.1 Thermal Oxidizer. The thermal oxidizer consists of a refractory-lined carbon steel mixing chamber and combustion chamber. Discrete burners are assumed. Enviroscience assumed a 10 percent heat loss from the combustion chamber for all combustion temperatures and design categories.[32]

5.2.1.2 Ductwork[33,48]. The ductwork used in the Enviroscience estimates consists of 150 ft of round-steel inlet with four ells, one expansion joint, and one damper with control. Enviroscience indicated that considerably more ductwork may be required in some cases. This analysis incorporates an additional 150 feet of ductwork, along with 250 feet of pipe rack support for the ductwork. The adjusted ductwork length of 300 feet was based on specifications provided by The Industrial Risk Insurers (IRI), a group which presents recommended distances for safely locating combustion sources from process units. The IRI safety recommendation for processes such as those found within the SOCMI is 200 feet. An additional 100 feet was added to the IRI safety recommendation to account for routing the stream around equipment before routing it away from the process unit.

The pipe rack costs are based on June 1982. In order to convert to June 1980 costs, a deescalation factor of 0.928 was used. This factor is the ratio of the Chemical Engineering M&S equipment cost index for the second quarter, 1982, to that for the second quarter, 1980. The additional

TABLE 5-5. TOTAL INSTALLED CAPITAL COST EQUATIONS AS A FUNCTION OF OFFGAS FLOWRATE[30,31]

Category	Maximum Flowrate Per Unit (Thousand) (scm/min)	Fabricated Equipment Cost Escalation Factor	Retrofit Correction Factor	C1	C2	C3
A1	0.70	1.056	1.625	803.11	12.83[a]	0.88
A2	0.70	1.056	1.625	786.61	12.44[a]	0.88
B	1.35	1.056	1.625	259.88	4.91	0.88
C	1.35	1.056	1.625	297.99	2.84	0.88
D	1.19	1.056	1.625	236.35	3.23	0.88
E[b]	1.19	1.056	1.625	236.35	3.23	0.88

Total Installed Capital Cost ($1000) = (# of Units) x (Escalation Factor) x (Retrofit Factor) x (C1 + C2 x (Flowrate per equipment unit in scm/min ÷ Design Vent Size Factor)^{C3})[c] + pipe rack cost[c] + additional ductwork cost.[d]

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[a] Flowrate correction factor of $1.12 = (1.14)^{0.88}$ incorporated into Coefficient C2.

[b] Dilution flowrate is used in capital cost equation.

Dilution flowrate = (design flowrate) x (original heating value) ÷ (3.6 MJ/scm).

[c] Pipe rack cost ($1,000) = (pipe rack length) x (cost per unit length) x (installation factor) x (pipe rack deescalation factor) x (retrofit correction factor) ÷ 1,000 $(\$/10^3\$)$ = 250[ft.] x 32.045[$/ft.] x 1.0873 x 0.928 x 1.625 ÷1,000$(\$/10^3)$.

[d] Additional ductwork cost = (ductwork length) x (cost per unit length) x (ductwork escalation factor) x (retrofit correction factor) x (installation factor) = 150(ft.)

$$\times \left[\frac{(\text{Flowrate} \times 35.314 \times 4)^{0.5}}{.95 \times 2000 \times 3.42} \times 12 \times 1.37 - 176\right] (\$/\text{ft.}) \times 1.364 \times 1.625 \times 1.087$$

$\div$ 1000 $(\$/10^3\$)$.

TABLE 5-6. INSTALLED CAPITAL COSTS FOR A SELECTED HYPOTHETICAL VENT STREAM IN EACH DESIGN CATEGORY[30,31]

Category	Offgas Heating Value (MJ/scm)	Vent Stream Design Flowrate (scm/min)	Number of Equipment Units	Dilution-Corrected Flowrate Through Each Equipment Unit (scm/min)	Overall System Installed Capital Cost[a] ($1000)
A1	0.74	344	1	344	5,169
A2	4.52	344	1	344	5,025
B	0.12	344	1	344	1,914
C	1.19	344	1	344	1,373
D	2.75	344	1	344	1,382
E	4.8	344	1	452	1,992
B, Two Equipment Units	0.12	2,400	2	1,200	9,988

[a] Including all auxiliary equipment.

ductwork costs are based on June 1977. Similarly, an escalation factor of 1.364 was used to transform these costs to June 1980. This escalation represents the Chemical Engineering M&S equipment cost index for the second quarter, 1977, to that for the second quarter, 1980.

5.2.1.3 Fans[34]. Fans are included for both offgas and combustion air. Costs for motors and starters are included. The offgas flowrate, combustion air flowrate (calculated from the flue gas to offgas flow ratio) and pressure drop of the thermal oxidizer are used to calculate fan sizes. For vent streams in Category A, which require flue gas scrubbing, the pressure drop across the scrubber is also considered.

5.2.1.4 Stack[35]. The stack design height is 80 ft. A linear gas velocity of 15 m/sec (3000 ft/min) is assumed in calculation of the cross-sectional area.

5.2.2 Categories A1 and A2

Streams in Categories A1 and A2 require flue gas quenching and scrubbing to remove corrosive hydrogen chloride. A waste heat boiler is employed for heat recovery prior to quenching.

5.2.2.1 Waste Heat Boiler[36]. An overall heat transfer coefficient of 0.16 $\text{MJ/(hr}\cdot\text{m}^2\cdot{}^\circ\text{C)}$ (8 $\text{Btu/(hr}\cdot\text{ft}^2\cdot{}^\circ\text{F))}$ is assumed for the boiler. Steam is generated at 120°C (250°F) and a pressure of 1.7 MN/m^2 (250 psi). For 60 percent heat recovery, the ratio of heat exchange surface area to flue gas flowrate is 0.89 $\text{m}^2\text{/scm}$ (0.27 $\text{ft}^2\text{/scfm}$).

5.2.2.2 Scrubber[37]. The scrubber column design is based on 36 ft of packing. The liquid-to-gas ratio is assumed to be 10. A superficial vapor velocity of three ft/sec was used for determining the column diameter.

5.2.2.3 Quench Chamber[38]. The quench chamber design location is the lower part of the scrubber column. It has the same diameter as the scrubber column. A one second flue gas retention was assumed. In reducing the flue gas temperature to the adiabatic saturation temperature of the scrubbing agent, considerable water is vaporized, increasing the gas flow through the scrubber. The ratio of quenched to unquenched flue gas flowrate (both standard) is 1.67 at 1100°C (2000°F).

5.2.3 Category B[39]

Vent streams in Category B employ 70 percent recuperative heat recovery. The heat exchanger tubes are constructed of carbon steel, except for the first few passes. It is necessary to construct the tube regions which experience a flue gas temperature between 820 and 870°C (1500 and 1600°F) of heat-resistant nickel alloy. An overall heat transfer coefficient of 0.08 $\text{MJ/hr}\cdot\text{m}^2\cdot\text{sec)}$ (4 $\text{Btu/(hr}\cdot\text{ft}^2\cdot{}^\circ\text{F)}$ is assumed for the heat exchanger. This assumption is deliberately low, and hence the heat exchanger is deliberately over-designed to some degree. For 70 percent heat recovery, the ratio of heat exchange surface area to flue gas flowrate is 2.7 $\text{m}^2\text{/scm}$

(0.83 ft^2/scfm). Recuperative heat recovery reduces both the natural gas and combustion air requirements of the thermal oxidizer. Therefore the required combustion chamber volume is reduced. For 70 percent heat recovery, the combustion chamber size reduction factor is 0.667 (corresponding to a 33 percent reduction in system size relative to no heat recovery).

5.2.4 Category C[40]

Vent streams in Category C are assumed to preheat the combustion air only, due to insurance requirements for safe handling of offgas with VOC concentrations above 25 percent of LEL in air. Thirty-four percent heat recovery is assumed. Materials of construction and overall heat transfer coefficient are the same as in Category B. For 34 percent heat recovery, the ratio of heat exchanger surface area to flue gas flowrate is 1.2 m^2/scm (0.36 ft^2/scfm). The combustion chamber size adjustment factor is 0.81 (corresponding to a 19 percent reduction in system size relative to no heat recovery).

5.2.5 Category D

Due to their high heating value, vent streams in Category D determine their own combustion temperature. A temperature as high as 980°C (1800°F) may be reached. Therefore, preheating of the offgas is not economically advantageous, nor is it technically feasible at temperatures above 870°C (1600°F). It was not assumed that any process with offgas in Category D could use generated steam, and therefore no waste heat boiler was included in the design. The combustion chamber design takes into account the extra refractory and internal volume required by the higher incineration temperature.

5.2.6 Category E

Vent streams in Category E are assumed to be sufficiently diluted prior to combustion that the resultant offgas heating value is 3.6 MJ/scm ([illegible] Btu/scf), so that the flue gas temperature will not exceed 980°C (1800°F). The correction equations are:

1. New flowrate = (old flowrate) x (old heating value) ÷ (3.6 MJ/scm),
2. New % VOC = (old % VOC) x (old flowrate) ÷ (new flowrate), and
3. New heating value = 3.6 MJ/scm.

The same incinerator design is assumed as in Category D.

5.3 BASIS FOR ANNUALIZED COSTS[41-43]

The typical annualized costs consist of the direct expenses for operating labor, utilities, and maintenance materials and labor plus the indirect costs for overhead, supervisory labor, taxes, insurances, general administration, and the capital recovery charges. The utilities include natural gas and electricity. For Category A, scrubbing water, quench makeup water, and caustic are also included. Return on investment for the control equipment is not included. All the data required in the estimation of these cost factors and costs were obtained from References 41, 42, and 43. The annualized cost factors are given in Table 5-7. Those operating factors which vary with design category are given in Table 5-8. The equations used to calculate annualized costs are given in Table 5-9.

TABLE 5-7. ANNUALIZED COST FACTORS[41-43]

All Factors are Based on June 1980

Direct

Operating Labor: \$9.79/hr (Includes Overhead)

Operating Labor Factor: 2400 Man-hr/yr (Categories A1-A2)
2133 Man-hr/yr (Categories B-C)
1200 Man-hr/yr (Categories D-E)

Supervisory Labor: \$9.79/hr x (0.15)

Total Labor: [(\$9.79/hr x 1.15) + (0.03 of Total Installed Capital)]

Overhead Labor: 0.80 of Total Labor

Electricity: \$0.0362 /kWh

Natural Gas: \$4.16/GJ = \$4.03/10^3 scf

Heat Recovery Credit: \$4.16/GJ = \$4.03/10^3 scf

Quench Water Price: \$0.26/Thousand Gallons

Scrubbing Water Price: \$0.26/Thousand Gallons

Caustic Price: \$0.05145/lb[a]

Maintenance Labor Plus Materials Factor = 0.06 of Total Installed Capital

Indirect ("Capital Charges")

Interest Rate = i = 10%

Incinerator Lifetime = 10 Years = N

Capital Recovery Factor = $\frac{i\,(1 + i)^N}{(1 + i)^N - 1}$ = 0.163 of Total Installed Capital

Taxes, Insurance and Administrative Charges Factor = 0.04 of Total Installed Capital

Overall Capital Charges Factor = 0.203 of Total Installed Capital

Overall Taxes and Maintenance Factor = 0.10 of Total Installed Capital

Annual Operation = 8760 hr/yr

Average Capacity Utilization Factor for Air Oxidation Industry = 0.77[b] (Multiplied by Design Flowrate to Give Operating Flowrate)

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[a] Fifty percent liquid solution of caustic soda.

[b] Memo to Hurley, E., EEA, from Galloway, J., EEA. January 13, 1981. Average capacity utilization for the air oxidation industry.

TABLE 5-8. OPERATING FACTORS FOR EACH DESIGN CATEGORY[41-43]

Category	Minimum Net Heating Value (MJ/scm)	Maximum Net Heating Value (MJ/scm)	Ratio of Flue Gas Flow to Offgas Flow[a]	Heat Recovery Factor (MJ/scm)	Pressure Drop (Inches H_2O)[44,45]	Operating Labor Cost ($1,000/YR)	Natural Gas Use Coefficients			
							G0	G1	G2	G3
A1[b]	0	3.5	2.9	3.38	22[c]	23.50	0	4.56	-0.985	0
A2[b]	3.5	-	2.9	3.38	22[c]	23.50	0	0.329	0	0
B	0.	0.48	1.9	0	10[d]	20.88	0.425	0.666	-1.29	0.015
C	0.48	1.9	2.3	0	10[d]	20.88	0	2.39	-1.22	0
D	1.9	3.6	2.5	0	6[e]	11.75	0	0.183	0	0
E	3.6	-	2.5	0	6[e]	11.75	0	0.183	0	0

[a] Both at standard conditions.

[b] Offgas contains halogenated compounds.

[c] Includes 6 inches across the combustion chamber, 4 inches across the waste heat boiler, and 12 inches across the scrubber.

[d] Includes 6 inches across the combustion chamber and 4 inches across the recuperative heat exchanger.

[e] Across the combustion chamber.

TABLE 5-9. ANNUALIZED COST EQUATIONS[41-43]

Operating flowrate (scm/min) = (Design flowrate (scm/min) x Capacity Utilization Factor) ÷ 95

In the following Operating Cost and emissions equations, "flowrate" means the operating flowrate per equipment unit (dilution flowrate for Category E)

Natural Gas Used (TJ/yr) = $0.5256 \frac{\text{Million Min}}{\text{yr}}$ x G0 + Flowrate x (G1 +(G2 x Heating Value) + (G3 x Heating Value^2))

Natural Gas Cost ($1,000/yr) = Natural Gas Price ($/GJ) x Natural Gas Used (TJ/yr)

Operating Labor Cost ($1,000/yr) = Labor wage ($/man-hr) x Operating labor factor (man-hr/yr) ÷ 1,000

Supervisory Labor Cost ($1,000) = Operating Labor Cost ($1,000) x 0.15

Maintenance Labor Cost ($1,000) = Installed Capital ($1,000) x 0.03

Total Labor Cost ($1,000) = (Operating Labor Cost ($1,000) + Supervisory Labor Cost ($1,000) + Maintenance Labor Cost ($1,000))

Overhead Cost ($1,000) = Total Labor Cost ($1,000) x 0.80

Electricity Cost ($1,000/yr) = 0.0604 x Electricity Price ($/kWh) x Pressure Drop (inches H_2O) x flowrate (scm/min) x flue-gas/offgas ratio

Quench water cost ($1,000/yr) = Quench water price ($/thousand gal) x flowrate (scm/min) x 0.00886 x flue-gas/offgas ratio

Scrubbing water cost ($1,000/yr) = Scrubbing water price ($/thousand gal) x flowrate (scm/min) x 0.289 x flue-gas/offgas ratio

Caustic cost ($1,000/yr) = Caustic Price ($/lb) x flowrate (scm/min) x 17.17 x flue-gas/offgas ratio

Heat recovery credit ($1,000/yr) = Natural Gas Price ($/GJ) x Heat Recovery Factor (MJ/scm) x flowrate (scm/min) x 0.5256 (Million min/yr)

Taxes, Insurance and Maintenance Cost ($1,000/yr) = Installed Capital ($1,000) x Taxes and Maintenance Factor

Operating Cost ($1,000/yr) = Taxes, Insurance and Maintenance Cost ($1,000/yr) + Number of equipment units x [Gas Cost + Labor Cost + Electricity Cost + Quench Cost + Scrub Cost + Caustic Cost - Heat Recovery Credit]

Annualized Cost ($1,000/yr) = Operating Cost + Capital Recovery Factor x Capital Cost ($1,000)

Annual Emissions (Gg/yr) = Hourly Emissions (kg/hr) x 365 days/year x 24 hours/day x 1 Gg/10^6kg x Capacity Utilization Factor

Annual Emission reduction (Gg/yr) = Annual Emission (Gg/yr) x 0.98

Cost Effectiveness ($/Mg) = Annualized Cost ($1,000/yr) ÷ Annual Emission Reduction (Gg/yr)

5.3.1 Fuel Requirements[44,45]

IT Enviroscience developed natural gas use curves and tables from a detailed heat and material balance. The Enviroscience work was checked for vent streams with heating values at the cutoff points distinguishing design Categories B, C, D, and E, as well as for chlorinated streams (Categories A1 and A2). For these cutoff cases, the heat and material balance was completely redone, using a slightly different set of assumptions.[46] These different assumptions included that of no preheating of the offgas for Category C streams. In addition, it was assumed that offgas with a VOC content of X mole percent would have a methane content of 4X mole percent. The common assumptions are presented above in Section 5.1.3.

The results of the recalculations for the critical cases were essentially in agreement with the Enviroscience work. Because of the necessity of calculating fuel requirements and costs for the entire national statistical profile of 59 vent streams (discussed in Appendix B), detailed heat and mass balances were not done for each stream. Instead, equations were fitted to the Enviroscience tables and graphs of natural gas use. The coefficients of the fuel-use equation are given in Table 5-8.

Streams in Categories D and E have sufficient heating value that they require only a small amount of fuel, for flame stability. The fuel requirement for these streams was assumed to be equivalent to 0.19 MJ of natural gas heat per normal cubic meter of offgas, independent of offgas heating value. This fuel requirement was chosen because it is equivalent to that calculated according to the Category C fuel use equation for offgas with a heating value of 1.9 MJ/scm (which is the cutoff heating value distinguishing Categories C and D). Therefore, a composite graph of the fuel use equations for Categories C and D versus offgas heating value would not be discontinuous at the cutoff heating value.

For the chlorinated streams in Categories A1 and A2, Enviroscience did not develop heat and mass balance calculations for the designated combustion temperature of 1100°C, but only for higher temperatures. Therefore, the fuel requirements were interpolated from the curves for 980°C and 1200°C. A fuel use equation was fitted to this interpolated curve. This equation indicates that chlorinated offgas with a heating value greater than 3.5 MJ/scm requires primarily auxiliary fuel, for flame stability. At this critical heating value, according to the fuel use equation, the amount of fuel required per normal cubic meter of offgas is equivalent to 10 percent of the offgas heating value, which is a typical auxiliary fuel requirement.[47] This heating value constitutes the cutoff between design Categories A1 and A2. For Category A1, the fuel-use equation discussed above was employed. For Category A2, the fuel requirement was assumed to be equivalent to 0.35 MJ of natural gas heat per normal cubic meter of offgas, independent of offgas heating value.

The assumption of a maximum heat exchange efficiency of 70 percent may be conservative for some facilities. A thermal oxidation system employing regenerative heat recovery could achieve a primary heat exchange efficiency as high as 85 to 95 percent. Therefore, facilities able to employ such technology may have lower fuel requirements.

Several additional conservative assumptions are built into the fuel use equations. The most important is the assumption of no oxygen in the offgas. This leads to maximum combustion air requirements and a higher total incinerator inlet flow to be heated to the combustion temperature.

The natural gas price used in the cost equations was derived by taking the natural gas price projected for the year 1990 weighted geographically. This 1990 gas price was then deflated to 1980 dollars. The weighting scheme was developed by taking individual gas price projections for the year 1990 for each of the 10 EPA regions. These projections were weighted according to the percentage of the total air oxidation plant capacity located within each region. The 1990 natural gas price reflects the summation of the values for each region.

5.4 EMISSION CONTROL COSTS

This section discusses the estimated emission control costs associated with control by RACT of a typical vent stream for each design category. These emission control costs are given in Table 5-10. The control costs are broken down into detailed components, including all types of operating expenses, capital charges, and heat recovery credits.

5.4.1 Major Contributing Factors to Control Costs of Typical Streams

The primary contributors to the annualized costs for the typical chlorinated, dilute Category A1 stream shown in Table 5-10 are capital charges and caustic costs. These account for about 45 percent and 28 percent, respectively, of the total annualized costs. For the chlorinated, concentrated Category A2 stream shown in Table 5-10, capital charges and caustic costs account for about 214 percent and 135 percent, respectively, of the total annualized costs. The sum of the other contributors is negative due to the very large heat recovery credit. For the dilute Category B streams which employ 70 percent heat recovery to reduce fuel requirements, capital charges account for about 43 percent of the total annualized cost. The moderately dilute streams of Category C, which cannot employ preheating of the offgas because of safety considerations, have the highest energy requirements of any category. For the typical Category C stream shown in Table 5-10, gas costs account for about 55 percent of the total annualized cost, while capital charges account for about 28 percent. The VOC-rich streams in Category D require little fuel, and capital charges account for about 52 percent of the total annualized cost of the typical stream shown in Table 5-10. The very rich streams of Category E, which are conservatively assumed to be diluted to avoid exceeding a 980°C combustion temperature, consequently require a larger incinerator volume per standard cubic meter of offgas. For this reason and because of the greater gas expansion at the higher combustion temperature, capital charges account for about 50 percent of the total annualized cost of the typical stream shown in Table 5-10.

5.4.2 Variation of Control Costs with Changes in Offgas Parameters

The percentage of the total annualized cost due to capital charges increases as offgas flowrate decreases due to economics of scale. In

TABLE 5-10. TYPICAL EMISSION CONTROL COSTS FOR EACH DESIGN CATEGORY

Category	Typical Heating Value (MJ/scm)	Typical Flowrate (scm/min)	Installed Capital ($1,000)	Capital Charges ($1,000/yr)	Maintenance ($1,000/yr)	Heat Recovery Credit ($1,000/yr)	Natural Gas Costs ($1,000)	Caustic Costs ($1,000/yr)	Operating Costs ($1,000/yr)	Annualized Costs (1,000/yr)
A1	0.74	327	5,169	1,049	155	1,938	2,179	646	1,668[a]	2,509
A2	4.52	327	5,025	1,020	151	1,939	189	646	-341[a]	477
B	0.12	327	1,914	389	57	0	294	0	585	897
C	1.19	327	1,373	278	41	0	537	0	763	987
D	2.75	327	1,382	281	41	0	105	0	314	539
E	4.8	327	1,992	404	60	0	184	0	480	804

[a] Includes $646,000 of caustic costs.

contrast, utilities and operating labor are generally linear functions of flowrate. For a given chemical manufacturing process, flowrate is expected to be roughly proportional to capacity. Therefore, the percentage of total annualized costs due to capital charges is also expected to increase as capacity decreases.

Total annualized costs, as well as each contributing factor to them, are expected to be essentially equal for any two given streams with the same flowrate and heating value, but differing VOC contents. (Such streams would have counterbalancing differences in non-VOC combustibles content.)

Total annualized cost (for nonchlorinated streams) is expected to decrease as heating value increases through Categories B and C, reaching a minimum at the low-heating value end of Category D. Total annualized cost is expected to increase with increasing heating value through Categories D and E, due to greater combustion air and dilution air requirements and gas expansion at higher combustion temperatures. This increase is attributable to increased capital charges. For chlorinated Category A1 streams, total annualized cost decreases with increasing offgas heating value. Annualized costs of Category A2 streams are not expected to be particularly sensitive to variation in offgas heating value. Due to higher capital costs attributable largely to the scrubber, chlorinated streams are in general more costly to control than nonchlorinated ones.

5.5 COST EFFECTIVENESS

The cost-effectiveness values are defined as total annualized costs per annual Mg of VOC emissions controlled. The cost effectiveness is calculated with respect to baseline emissions. Uncontrolled emissions were defined as emissions from the primary absorber vent. The estimate baseline control fraction of 58 percent is derived in Appendix B. The cost effectiveness for selected vent streams of all design categories and with various offgas characteristics are given in Table 5-11.

5.5.1 Variation of Cost Effectiveness with Changes in Offgas Parameters

That portion of cost effectiveness attributable to utilities and operating labor is generally insensitive to variations in offgas flowrate or capacity. In contrast, that portion of cost effectiveness attributable to capital charges is expected to decrease with increasing flowrate. This effect is illustrated by the three Category B streams in Table 5-11 which vary only in offgas flowrate. However, vent streams with flowrates just large enough to require an additional control system unit will have a correspondingly higher cost effectiveness. The cost effectiveness of a Category B stream with a flowrate of 1,350 scm/min (the assumed maximum value) is expected to increase about 76 percent if two equipment units are employed.

Increases in VOC content decrease cost effectiveness in two ways. If non-VOC combustible content remains constant, heating value will increase with increasing VOC content, and that portion of cost effectiveness attributable to fuel requirements will in general decrease. Emission reduction is proportional to VOC content. Therefore, cost effectiveness is inversely proportional to VOC content (apart from the relation of heating value to VOC content). This effect is illustrated in Table 5-11 by the pairs of streams which differ from each other only in VOC content.

TABLE 5-11. COST EFFECTIVENESS FOR SELECTED STREAMS OF EACH DESIGN CATEGORY

Category	Characteristics	Net Heating Value (MJ/scm)	Hourly Emissions Rate (kg/hr)	Non-VOC Combustible Content (Volume Percent)	Operating Flowrate (scm/min)	Annualized Costs ($1,000/yr)	Annual Emissions (Gg/yr)	Annual Emission Reduction (Gg/yr)	Cost Effectiveness ($/Mg)
A1	Typical	0.74	130	1.5	327	2,509	0.88	0.86	2,917
A2	Typical	4.52	650	9.7	327	477	4.41	4.33	110
B	Typical	0.12	130	0	327	897	0.88	0.86	1,043
B	Low Emissions Rate	0.12	18	0.4	327	897	0.121	0.119	7,534
B	Low Flowrate	0.12	26	0	65	338	0.175	0.174	1,966
B	High Flowrate	0.12	960	0	2,400	5,294	6.48	6.35	817
C	Typical	1.19	130	2.7	327	987	0.88	0.86	1,148
C	High Emissions Rate	1.19	440	1.2	327	987	2.97	2.91	339
D	Typical	2.75	220	6.8	327	539	1.48	1.45	370
E	Typical	4.8	220	12.6	436	804	1.48	1.45	553

[a] Requires three equipment units.

Cost effectiveness has a significant dependence on non-VOC combustible content, although the relation is weaker than that between cost effectiveness and VOC content. Streams which differ in non-VOC combustible content but not in VOC content must have different heating values. Among vent streams in the statistical profile (discussed in Appendix B), variations in non-VOC combustible content are quite pronounced. Cost effectiveness generally decreases with an increase in heating value, if the VOC content is constant. However, cost effectiveness is expected to increase with increased heating values within the boundaries of design Categories B and C, due to the loss of potential heat recovery from the offgas. A cost-effectiveness increase is also expected with increased heating value through the range of Category E, due to the increasing dilution air requirements.

5.5.2 Total Resource Effectiveness (TRE) Index

The total resource effectiveness (TRE) index of a vent stream is defined as the cost effectiveness of the stream divided by $1,600/Mg. The TRE index is a convenient, dimensionless measure of the total resource burden associated with VOC control at a facility. It is independent of the general inflation rate. However, it does assume fixed relative costs of the various resources, except for natural gas (as discussed in Chapter 4).

The TRE index of a process vent stream can be estimated according to the following equation:

$$\mathrm{TRE} = \frac{1}{E}\ [a + b(\mathrm{FLOW})^{0.88} + c(\mathrm{FLOW}) + d(\mathrm{FLOW})(H_T) + e(\mathrm{FLOW}^{0.88})(H_T{}^{0.88}) + f\ (\mathrm{FLOW})^{0.5}]$$

where:

TRE = Total resource effectiveness index value.

FLOW = Vent stream flowrate (scm/min), at a standard temperature of 20°C.*,**

E = Hourly measured emissions in Kg/hr.*

H_T = Vent stream net heating value (MJ/sc [illegible]., where the net enthalpy per mole of offgas is based on combustion at 25°C and 760 mm Hg, but the standard temperature for determining the volume corresponding to one mole is 20°C, as in the definition of FLOW.*

a, b, c, d, e, and f are coefficients. The set of coefficients which apply to a process vent stream can be obtained from Table 5-12. These coefficients were obtained by substituting the numeric values for all variables, except offgas flowrate, heating value, and VOC content, in the cost and emissions equations given in Tables 5-5 and 5-9. The resulting equations were substituted into the cost-effectiveness equation given in Table 5-9, which was then indexed to a constant cost-effectiveness value as described above. The TRE index equation simplifies to the six terms shown

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*See Appendix H for reference methods and procedures.

**For a Category E stream, Flow should be replaced by "Flow x H_T/3.6" when associated with the f coefficient.

TABLE 5-12. COEFFICIENTS OF THE TOTAL RESOURCE-EFFECTIVENESS (TRE) INDEX EQUATION

A1. FOR CHLORINATED PROCESS VENT STREAMS, IF $0 \leq$ NET HEATING VALUE (MJ/scm) ≤ 3.5:

W = Vent Stream Flowrate (scm/min)	a	b	c	d	e	f
$W < 13.5$	48.73	0	0.404	-0.1632	0	0
$13.5 < W \leq 700$	42.35	0.624	0.404	-0.1632	0	0.0245
$700 < W \leq 1400$	84.38	0.678	0.404	-0.1632	0	0.0346
$1400 < W \leq 2100$	126.41	0.712	0.404	-0.1632	0	0.0424
$2100 < W \leq 2800$	168.44	0.747	0.404	-0.1632	0	0.0490
$2800 < W \leq 3500$	210.47	0.758	0.404	-0.1632	0	0.0548

A2. FOR CHLORINATED PROCESS VENT STREAMS, IF $3.5 <$ NET HEATING VALUE (MJ/scm):

W = Vent Stream Flowrate (scm/min)	a	b	c	d	e	f
$W < 13.5$	47.76	0	-0.292	0	0	0
$13.5 < W \leq 700$	41.58	0.605	-0.292	0	0	0.0245
$700 < W \leq 1400$	82.84	0.658	-0.292	0	0	0.0346
$1400 < W \leq 2100$	123.10	0.691	-0.292	0	0	0.0424
$2100 < W \leq 2800$	165.36	0.715	-0.292	0	0	0.0490
$2800 < W \leq 3500$	206.62	0.734	-0.292	0	0	0.0548

B. FOR NONCHLORINATED PROCESS VENT STREAMS, IF $0 \leq$ NET HEATING VALUE (MJ/scm) ≤ 0.48:

W = Vent Stream Flowrate (scm/min)	a	b	c	d	e	f
$W < 13.5$	19.05	0	0.113	-0.214	0	0
$13.5 < W \leq 1350$	16.61	0.239	0.113	-0.214	0	0.0245
$1350 < W \leq 2700$	32.91	0.260	0.113	-0.214	0	0.0346
$2700 < W \leq 4050$	49.21	0.273	0.113	-0.214	0	0.0424

C. FOR NONCHLORINATED PROCESS VENT STREAMS, IF $0.48 <$ NET HEATING VALUE (MJ/scm) ≤ 1.9:

W = Vent Stream Flowrate (scm/min)	a	b	c	d	e	f
$W < 13.5$	19.74	0	0.400	-0.202	0	0
$13.5 < W \leq 1350$	18.30	0.138	0.400	-0.202	0	0.0245
$1350 < W \leq 2700$	36.28	0.150	0.400	-0.202	0	0.0346
$2700 < W \leq 4050$	54.26	0.158	0.400	-0.202	0	0.0424

D. FOR NONCHLORINATED PROCESS VENT STREAMS, IF $1.9 <$ NET HEATING VALUE (MJ/scm) ≤ 3.6:

W = Vent Stream Flowrate (scm/min)	a	b	c	d	e	f
$W < 13.5$	15.24	0	0.033	0	0	0
$13.5 < W \leq 1190$	13.63	0.157	0.033	0	0	0.0245
$1190 < W \leq 2380$	26.95	0.171	0.033	0	0	0.0346
$2380 < W \leq 3570$	40.27	0.179	0.033	0	0	0.0424

E. FOR NONCHLORINATED PROCESS VENT STREAMS, IF $3.6 <$ NET HEATING VALUE (MJ/scm):

W = Dilution Flowrate (scm/min)	a	b	c	d	e	f
$W < 13.5$	15.24	0	0	0.0090	0	0
$13.5 < W \leq 1190$	13.63	0	0	0.0090	0.0503	0.0245
$1190 < W \leq 2380$	26.95	0	0	0.0090	0.0546	0.0346
$2380 < W \leq 3570$	40.27	0	0	0.0090	0.0573	0.0424

above. At least two of the equation terms equal zero for vent streams in any design category. The term of the gas use equation proportional to squared heating value is sufficiently insignificant that it was ignored in constructing the simplified equation and table of coefficients.

Table 5-12 is divided into the six design categories for control equipment. Under each design category listed in the table, there are several intervals of offgas flowrate. Each flowrate interval is associated with a different set of TRE equation coefficients. The first flowrate interval in each design category applies to vent streams with a flowrate smaller than that corresponding to the smallest control equipment system easily available without special custom design. The remaining flowrate intervals in each design category apply to vent streams which would be expected to use one, two, three, four, or five sets of control equipment, respectively.

5.5.3 TRE Index Cutoff Value and Impacts of the RACT Recommendation

The RACT recommendation is based on incineration of those process vent streams with an associated TRE index value of less than 1.0. This TRE index cutoff value corresponds to a cost effectiveness of $1600 per Mg of VOC destroyed. Under this RACT recommendation, three of the selected streams presented in Table 5-11 would not reduce VOC emissions. These are the chlorinated, dilute Category A1 stream and the Category B stream with a very low VOC content and the Category B stream with a low flowrate. Streams with very low flowrates would tend to exceed the TRE index cutoff value, even if their fuel requirements were small. Appendix D gives the procedure necessary for converting the TRE index value of a facility to facility cost effectiveness in $/Mg.

The estimated overall impacts of RACT are presented in Table 5-13. The RACT involves a 98 percent VOC reduction for the estimated 14 facilities which would control VOC emissions. An estimated 33 facilities would not control VOC emissions under RACT. These impacts were projected assuming the applicability of the statistical profile of offgas parameters (discussed in Appendix B) to the 47 existing air oxidation facilities located in ozone nonattainment areas. Any facilities in the profile that now use combustion control or have changed processes were automatically considered not subject to additional VOC emissions controls under RACT. The estimated overall annualized cost associated with RACT is $30 million/yr and the estimated overall capital cost is $30 million.

TABLE 5-13. ESTIMATED IMPACTS OF RACT[a]

Cutoff Total Resource Effectiveness Index	Cutoff Cost Effectiveness ($/Mg)[b,c]	Number of Sources Affected[d]	National Emissions After Control By RACT[e] (Gg/yr)	Percent Emission Reduction Over Baseline	National Energy Impact (TJ/yr)[d]	Overall Annualized Cost (Million $/yr)[c,d]	Overall Installed Capital Cost (Million $)[c,d]
1.0	1,600	14	19	53	5,000	30	30

[a] Assuming applicability of the statistical profile of offgas parameters to the 47 existing air oxidation facilities located in ozone nonattainment areas.

[b] Highest cost effectiveness for any plant which would control VOC under RACT. Plants with a higher cost effectiveness would not control VOC under RACT.

[c] June, 1980 dollars.

[d] RACT involves 98 percent VOC reduction from baseline levels for those facilities which would control VOC emissions. However only an estimated 14 of the 47 plants would control VOC emissions under RACT.

[e] RACT would reduce national emissions over baseline by 21 Gg/yr (from 40 Gg/yr to 19 Gg/yr).

5.6 REFERENCES FOR CHAPTER 5

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APPENDIX A. EMISSION SOURCE TEST DATA

APPENDIX A: EMISSION SOURCE TEST DATA

The purpose of this appendix is to describe results of tests of volatile organic compound (VOC) emissions reduction by thermal incineration. These test results were used in the development of the control techniques guideline (CTG) document for air oxidation processes of the synthetic organic chemicals manufacturing industry (SOCMI). Background data and detailed information which support the emission levels achievable are included.

Section A.1 of this appendix presents the VOC emissions test data including individual test descriptions. Section A.2 provides a summary of NO_x emissions from some of the tests. Section A.3 consists of comparisons of various test results and a discussion exploring and evaluating the similarities and differences of these results.

A.1 VOC EMISSIONS TEST DATA

The tests were aimed at evaluating the performance of thermal incinerators when used under varied conditions on the air oxidation process waste streams. The results of this study indicate that 98 percent VOC reduction or 20 ppmv by compound exit concentration, whichever is less stringent, is the highest control level currently achievable by all new incinerators, considering available technology, cost, and energy use.[1] This level is expressed in both percent reduction and ppmv to account for the leveling off of exit concentrations as inlet concentrations drop. This level can be achieved by incinerator operation at conditions which include a maximum of 1600°F and 0.75 second residence time. The 98 percent level can frequently be achieved at lower combustion temperatures.

Three sets of test data are available. These sets consist of field unit data from tests conducted by EPA and by chemical companies and of lab-scale incinerator data from tests by Union Carbide.

A.1.1 Chemical Company Test Data

These data are from tests performed by chemical companies on incinerators at three air oxidation units: the Petro-tex oxidative butadiene unit at Houston, Texas, the Koppers maleic anhydride unit at Bridgeville, Pennsylvania, and the Monsanto acrylonitrile unit at Alvin, Texas.

A.1.1.1 Petro-Tex Test Data[2]

1. Facility and Control Device - The Petro-tex incinerator for the "Oxo" butadiene process is designed to treat 48,000 scfm waste gas containing about 4000 ppm hydrocarbon and 7000 ppm carbon dioxide. The use of the term hydrocarbon in this discussion indicates that besides VOC, it may include non-VOC such as methane. The waste gas treated in this system results from air used to oxidize butene to butadiene. The waste gas, after butadiene has been recovered in an oil absorption system, is combined with other process waste gas and fed to the incinerator. The waste gas enters the incinerator between seven vertical Coen duct burner assemblies. The incinerator design incorporates flue gas recirculation and a waste heat

boiler. The benefit achieved by recirculating flue gas is to incorporate the ability to generate a constant 100,000 lbs/hr of 750 psi steam with variable waste gas flow.[3] The waste gas flow can range from 10 percent to 100 percent of design production rate.

The incinerator measures 72 feet by 20 feet by 8 feet, with an average firebox cross-sectional area of 111 square feet. The installed capital cost was $2.5 million.

The waste gas stream contains essentially no oxygen; therefore, significant combustion air must be supplied. This incinerator is fired with natural gas which supplies 84 percent of the firing energy. The additional required energy is supplied by the hydrocarbon contamination of the waste gas stream. Figure A-1 gives a rough sketch of this unit.

2. Sampling and Analytical Techniques Waste Gas

The waste gas sampling was performed with integrated bags. The analysis was done on a Carle analytical gas chromatograph having the following columns:

1. 6-ft OPN/PORASIL^R (80/100).
2. 40-ft 20 percent SEBACONITRILE^R on gas chrom. RA 42/60.
3. 4-ft PORAPAK^R N 80/100.
4. 6-ft molecular sieve bx 80/100.

Stack Gas

The stack gas samples are collected via a tee on a long stainless steel probe which can be inserted into the stack at nine different locations. These gas samples are collected in 30-50 cc syringes.

The gas samples are then transferred to a smaller 1 cc syringe via a small glass coupling device sealed at both ends with a rubber grommet. The 1-cc samples can then be injected into a chromatograph for hydrocarbon analysis. A Varian 1700 chromatograph is used, having a 1/8-in. x 6-ft column packed with 5A molecular sieves and a 1/4-in. x 4-ft column packed with glass beads connected in series with a bypass before and after the molecular sieve column, controlled by a needle valve to split the sample. The data are reported as ppm total HC, ppm methane, and ppm non-methane hydrocarbons (NMHC). The CO content in the stack is determined by using a Kitagawa sampling probe. The O_2 content in the stack is determined via a Teledyne O_2/combustible analyzer.

3. Test Results - Petro-tex has been involved in a modification plan for its "Oxo" incinerator unit after startup. The facility was tested by the company after each major modification was made to determine the impact of these changes on the VOC destruction efficiency. The incinerator showed improved performance after each modification and the destruction efficiency increased from 70 percent to well above 98 percent. Table A-1 provides a summary of these test results. The type of modifications made in the incinerator were as follows:

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Test data prior to these changes showed the incinerator was not destroying hydrocarbons as well as it should (VOC destruction efficiency as low as 70 percent), so the following changes were made:

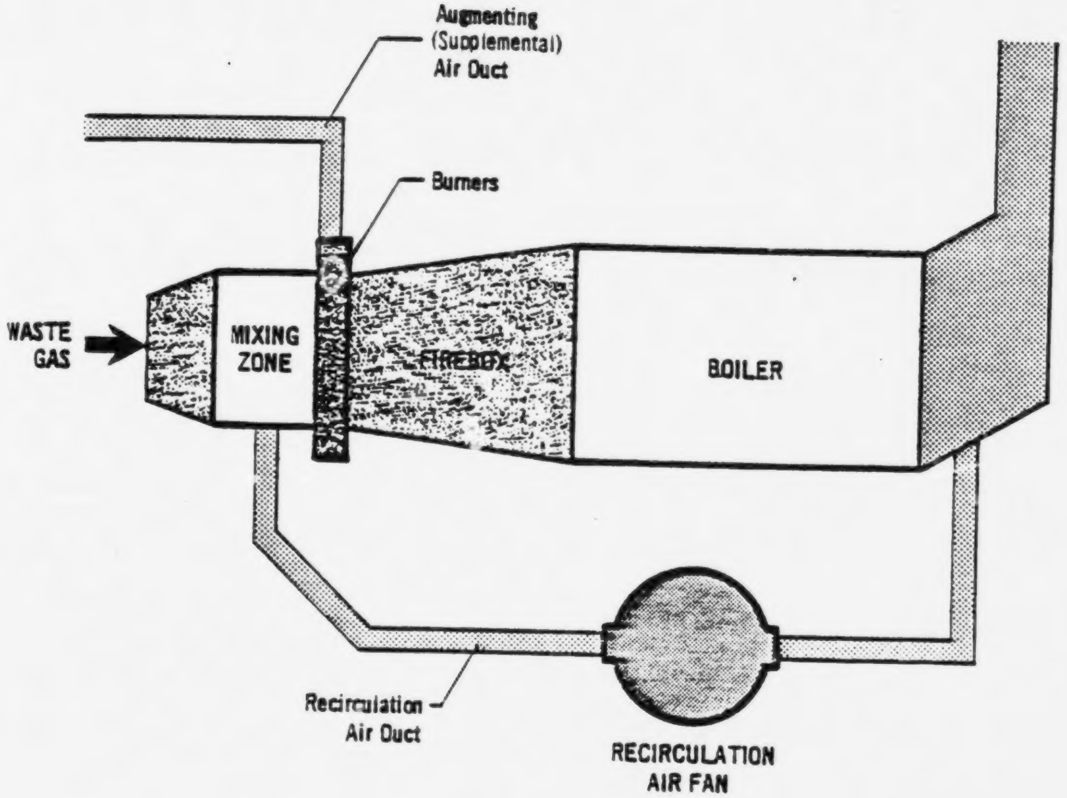

Augmenting
(Supplemental)
Air Duct
Burners
WASTE GAS
MIXING ZONE
FIREBOX
BOILER
Recirculation Air Duct
RECIRCULATION AIR FAN

Figure A–1. Petro-Tex oxo unit incinerator.

TABLE A-1. THERMAL INCINERATOR FIELD TEST DATA

Company & Location	Type of Process	Production Rate During Test Waste Gas Flow (Inlet) scfm	Number of Tests or Sets	Test Date	Supplemental Fuel & Amount Used (scfm)	Residence Time (Seconds)	Incineration Temperature (°F)	Inlet VOC (ppmv)	Outlet VOC (ppmv)	VOC Destruction Efficiency by Weight
Petro-tex Chemical Corp., Houston, TX	Butadiene	7,250	Set 1	5/25/77	Natural Gas 1400	0.6	1400	10,300	1000	70.3
		15,617	Set 2	9/09/77	1467	0.6	1400	10,650	215	94.1
		20,750	Set 3	12/01/77	900	0.6	1400	10,650	215	94.1
		15,867	Set 4	4/19/78	1175	0.6	1400	10,300	10	99.6
		12,500	Set 5	9/27/78	1176	0.6	1400	10,300	10	99.6
		Avg. Combustion Air: 49,333								
Koppers Co., Inc. Bridgeville, PA	Maleic Anhydride	33,200 Air: 8000	Set 1	11/02/77	Natural Gas	0.6	"Below 2000"	834	7	98.96
		24,200 Air: 2000	Set 2	11/16/77		0.6		834	8	98.96
Monsanto Chemical Intermediates Co., Alvin, TX	Acrylonitrile	75,000 (Avg.)	Unit 1	12/16/77	Natural Gas	N/A	Confidential	Confidential	25	>99
			Unit 2	12/16/77		N/A			47	>99
Denka, Houston, TX	Maleic Anhydride	33,000 (70% of total capacity)	3	3/21/78	1060 (gas)	0.6	1400	950	13	98.5
				3/22/78	1060	0.6	1400	950	13	98.5
				3/23/78	1060	0.6	1400	950	13	98.5
Rohm & Haas, Deer Park, TX	Acrylic Acid & Esters	Each 52,500 (12,500 tank farm vent (TVF)) (40,000 oxidizer vent (OXV))	Set 1 3	3/78	900 (gas)	1.0	1425	TVF 2,580 OXV 11,600	1330	82.6
			Set 2 4	3/78	900	1.0	1510	TVF 2,600 OXV 12,800	150	98.3
			Set 3 1	3/78	900	1.0	1545	TVF 2,410 OXV 12,200	25	99.7
Union Carbide Corp., Taft, LA	Acrylic Acid & Acrylate Esters	20,600	Set 1 6	12/78	Natural Gas	2-3	1160	11,900	243	96.1
			Set 2 3	12/78		2-3	1475	11,900	10	99.9

1. Moved the duct burner baffles from back of the burner to the front.
2. Installed spacers to create a continuous slot for supplemental air to reduce the air flow through the burner pods.
3. Installed plates upstream of the burners so that ductwork matches burner dimensions.
4. Cut slots in recycle duct to reduce exit velocities and improve mixing with Oxo waste gas.
5. Installed balancing dampers in augmenting (supplemental) air plenums, top and bottom.
6. Installed balancing dampers in three of the five sections of the recycle duct transition.
7. Cut opening in the recirculation duct to reduce the outlet velocities.

March 1978

After the November changes were made, a field test was made in December 1977, which revealed that the incinerator VOC destruction efficiency increased from 70.3 percent to 94.1 percent. However, it still needed improvement. After much discussion and study the following changes were made in March 1978:

1. Took the recirculation fan out of service and diverted the excess forced draft air into the recirculation duct.
2. Sealed off the 5-1/2-in. wide slots adjacent to the burner pods and removed the 1/2-in. spacers which were installed in November 1977.
3. Installed vertical baffles between the bottom row of burner pads to improve mixing.
4. Installed perforated plates between the five recirculation ducts for better Oxo waste gas distribution.
5. Cut seven 3-in. wide slots in the recycle duct for better secondary air distribution.

July 1978

After the March 1978 changes, a survey in April 1978 showed the Oxo incinerator to be performing very well (VOC destruction efficiency of 99.6 percent) but with a high superheat temperature of 850°F. So, in July 1978, some stainless steel shields were installed over the superheater elements to help lower the superheat temperature. A subsequent survey in September 1978, showed the incinerator to still be destructing 99.6 percent VOC and with a lower superheat temperature (750°F).

This study pointed out that mixing is a critical factor in efficiency and that incinerator adjustment after startup is the most feasible and efficient means of improving mixing and thus, the destruction efficiency.

A.1.1.2 Koppers Test Data[4]

1. Facility and Control Device - The Koppers incinerator is actually a boiler adapted to burn gaseous wastes from maleic anhydride unit. The boiler is designed to operate at a temperature of 2000°F and a residence

time of 0.6 second. Current operating parameters have not been measured, but it is the company's judgment that the boiler now operates somewhat below 2000°F. The flowrate of waste gas to the boiler is usually 32,000 scfm and contains 350 lbs/hr benzene, 2850 lbs/hr carbon monoxide, 22,100 lbs/hr oxygen, 6434 lbs/hr water, and 105,104 lbs/hr nitrogen. While these values are typical for the system, they vary throughout the production cycle. The boiler is fired with natural gas.

2. Sampling and Analytical Techniques - Different methods were used for inlet and outlet sampling. Although integrated samples were used for the outlet, gas bottle samples were used for the inlet. Such a sampling technique would likely give a low bias to the measured inlet VOC concentration.

The inlet concentration was taken to be the average of all maleic reactor offgas measurements made. There were four samples taken, and the results were 600 ppmv, 1172 ppmv, 600 ppmv, and 964 ppmv for an average of 834 ppmv benzene. (These values are not boiler inlet values since they were collected prior to the introduction of the additional combustion air.) This wide range of benzene values indicates the great deal of variability inherent in efficiency calculations employing such a sampling technique.

For the June 1978 tests, samples of stack gas were taken in glass bottles by plant chemists and analyzed at Koppers' Monroeville Research Center by direct injection to a gas chromatograph with flame ionization detector. The November 1977 method used specially-designed charcoal adsorption tubes, instead of impingers, in a United States Environmental Protection Agency-type sampling train. The charcoal was eluted with CS_2 and the eluent analyzed by gas chromatography.

3. Test Results - One test run of the Koppers data indicates 97.2 percent efficiency at 1800°F. However, the entire Koppers test is disregarded as not demonstrably accurate because of the poor sampling technique. Grab samples employed in obtaining inlet gas could give a low bias to the measured inlet VOC concentration. Therefore, the calculated VOC destruction efficiency would be artificially low. Table A-1 provides a summary of these test results.

A.1.1.3 Monsanto Test Data[5]

1. Facility and Control Device - The Monsanto incinerator burns both liquid and gaseous wastes from the acrylonitrile unit and is termed an absorber vent thermal oxidizer. Two identical oxidizers are employed. The primary purpose of the absorber vent thermal oxidizers is hydrocarbon emission abatement.

Acrylonitrile is produced by feeding propylene, ammonia, and excess air through a fluidized, catalytic bed reactor. In the process, acrylonitrile, acetonitrile, hydrogen cyanide, carbon dioxide, carbon monoxide, water, and other miscellaneous organic compounds are produced in the reactor. The columns in the recovery section separate water and crude acetonitrile as liquids. Propane, unreacted propylene, unreacted air components, some unabsorbed organic products, and water are emitted as a vapor from the absorber column overhead. The crude acrylonitrile product is further refined in the purification section to remove hydrogen cyanide and the remaining hydrocarbon impurities.

The organic waste streams from this process are incinerated in the absorber vent thermal oxidizer at a temperature and residence time sufficient to reduce stack emissions below the required levels. The incinerated streams include (1) the absorber vent vapor (propane, propylene, CO, unreacted air components, unabsorbed hydrocarbons), (2) liquid waste acetonitrile (acetonitrile, hydrogen cyanide, acrylonitrile), (3) liquid waste hydrogen cyanide, and (4) product column bottoms purge (acrylonitrile, some organic heavies). The two separate acrylonitrile plants at Chocolate Bayou employ identical thermal oxidizers.

Each thermal oxidizer is a horizontal, cylindrical, saddle-supported, end-fired unit consisting of a primary burner vestibule attached to the main incinerator shell. Each oxidizer measures 18 feet in diameter by 36 feet in length.

The thermal oxidizer is provided with special burners and burner guns. Each burner is a combination fuel-waste liquid unit. The absorber vent stream is introduced separately into the top of the burner vestibule. The flows of all waste streams are metered and sufficient air is added for complete combustion. Supplemental natural gas is used to maintain the operating temperature required to combust the organics and to maintain a stable flame on the burners during minimum gas usage. Figure A-2 gives a plan view of the incinerator.

2. Sampling and Analytical Techniques

Feed Stream and Effluent

The vapor feed streams (absorber vent) to the thermal oxidizer and the effluent gas stream are sampled and analyzed using a modified analytical reactor recovery run method. The primary recovery run methods are Sohio Analytical Laboratory Procedures.

The modified method involves passing a measured amount of sample gas through three scrubber flasks containing water and catching the scrubbed gas in a gas sampling bomb. The samples are then analyzed with a gas chromatograph and the weight percent of the components is determined.

Stack Gas

Figure A-3 shows the apparatus and configuration used to sample the stack gas. It consists of a line of the sample valve to the small water-cooled heat exchanger. The exchanger is then connected to a 250 ml sample bomb used to collect the unscrubbed sample. The bomb is then connected to a pair of 250 ml bubblers, each with 165 ml of water in it. The scrubbers, in turn, are connected to another 250 ml sample bomb used to collect the scrubbed gas sample which is connected to a portable compressor. The compressor discharge then is connected to a wet test meter that vents to the atmosphere.

After assembling the apparatus, the compressor is turned on and it draws gas from the stack and through the system at a rate of 0.2 ft^3/min. Sample is drawn until at least 10 ft^3 have passed through the scrubbers. After 10 ft^3 has been scrubbed, the compressor is shutdown and the unscrubbed bomb is analyzed for CH_4, C_2's, C_3H_6, and C_3H_8, the scrubbed bomb is analyzed for N_2, air, O_2, CO_2, and CO, and the bubbler liquid is analyzed for acrylonitrile, acetonitrile, hydrogen cyanide, and total organic carbon. The gas samples are analyzed by gas chromatography. For the liquid samples,

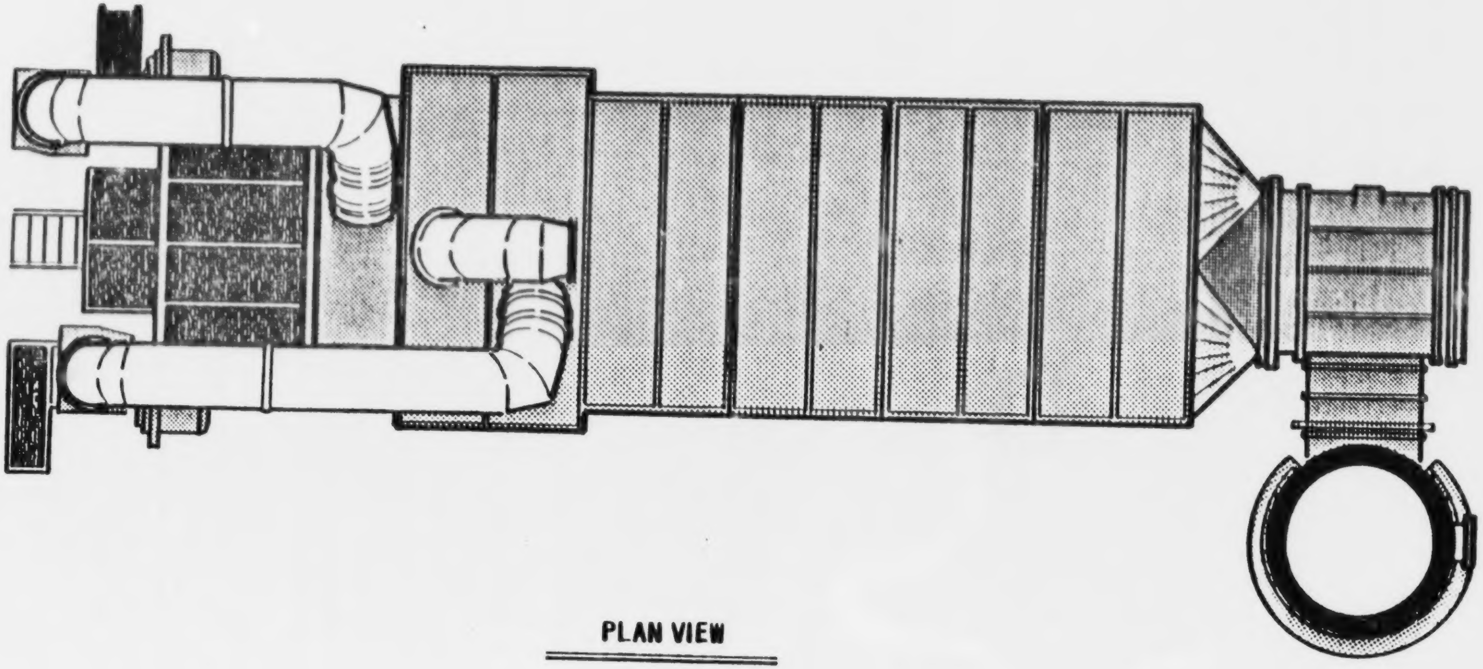
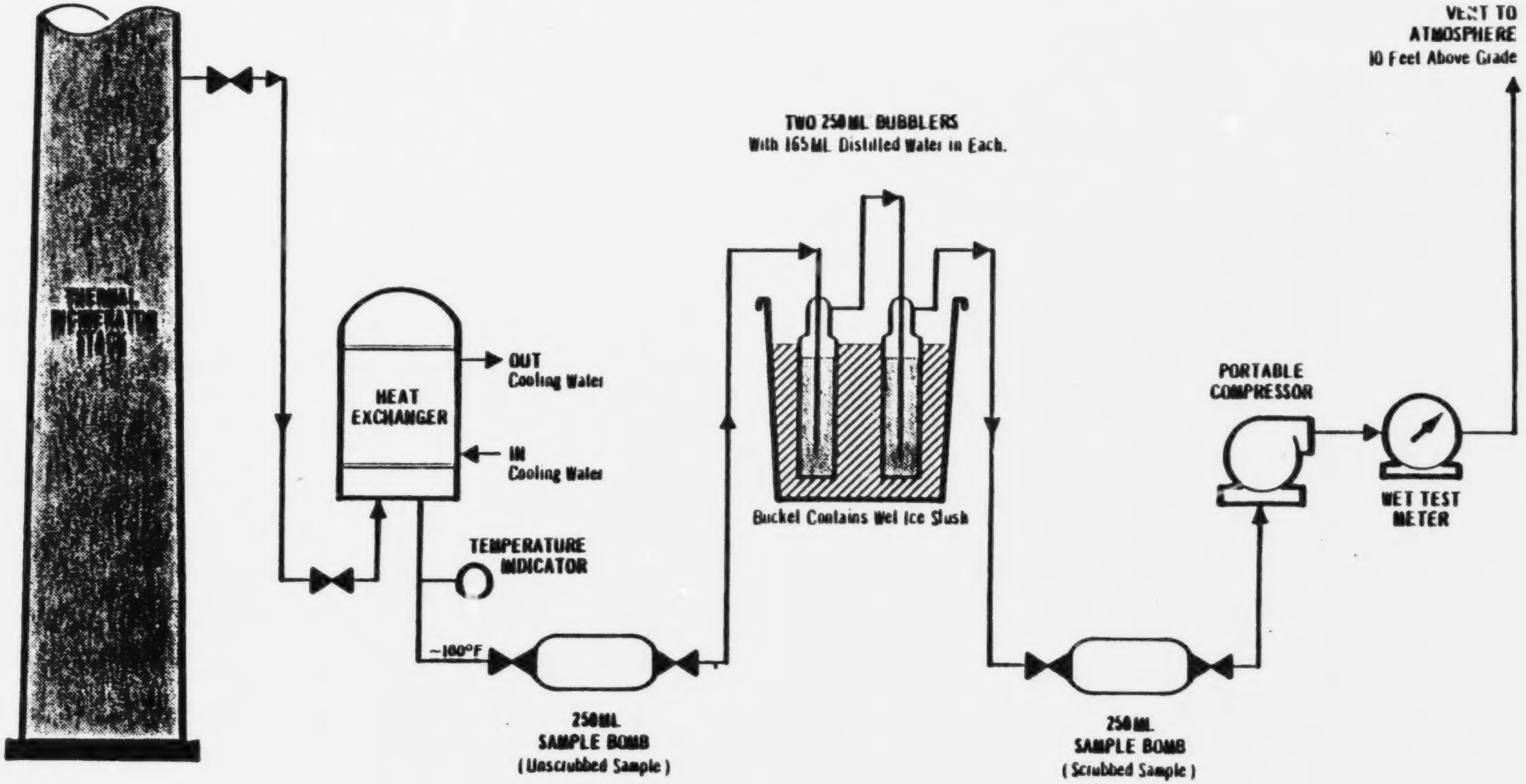


Figure A–2. Off-gas incinerator, Monsanto Co., Chocolate Bayou Plant.


VENT TO
ATMOSPHERE
10 Feet Above Grade
TWO 250ML BUBBLERS
With 165ML Distilled Water in Each.
THERMAL
INCINERATOR
OUT
Cooling Water
HEAT
EXCHANGER
IN
Cooling Water
TEMPERATURE
INDICATOR
~100°F
Bucket Contains Wet Ice Slush
PORTABLE
COMPRESSOR
WET TEST
METER
250ML
SAMPLE BOMB
(Unscrubbed Sample)
250ML
SAMPLE BOMB
(Scrubbed Sample)

NOTE: From Exchanger Process Outlet, All Lines are Vacuum Tubing.

Figure A–3. Thermal incinerator stack sampling system.

acrylonitrile and acetonitrile are analyzed by gas chromatography; hydrogen cyanide (HCN) is by titration; and total organic carbon (TOC) is by a carbon analysis instrument.

3. Test Results - Monsanto's test results show efficiencies well above 98 percent; however, the parameters at which it is achieved are confidential. All other known conditions are presented in Table A-1.

A.1.2 Environmental Protection Agency (EPA) Test Data

The EPA test study represents the most in-depth work available. These data show the combustion efficiencies for full-scale incinerators on air oxidation vents at three chemical plants. Data include inlet/outlet tests on large incinerators, two at acrylic acid plants, and one at a maleic anhydride plant. The tests measured inlet and outlet VOC by compound at different temperatures, and the reports include complete test results, process rates, and test method descriptions. The three plants tested are the Denka, Houston, Texas, maleic anhydride unit and the Rohm and Haas, Deer Park, Texas, and Union Carbide, Taft, Louisiana, acrylic acid units. The data from Union Carbide include test results based on two different incinerator temperatures. The data from Rohm and Haas include results for three temperatures. In all tests, bags were used for collecting integrated samples and a GC/FID was used for organic analysis.

A.1.2.1 Denka Test Data[6]

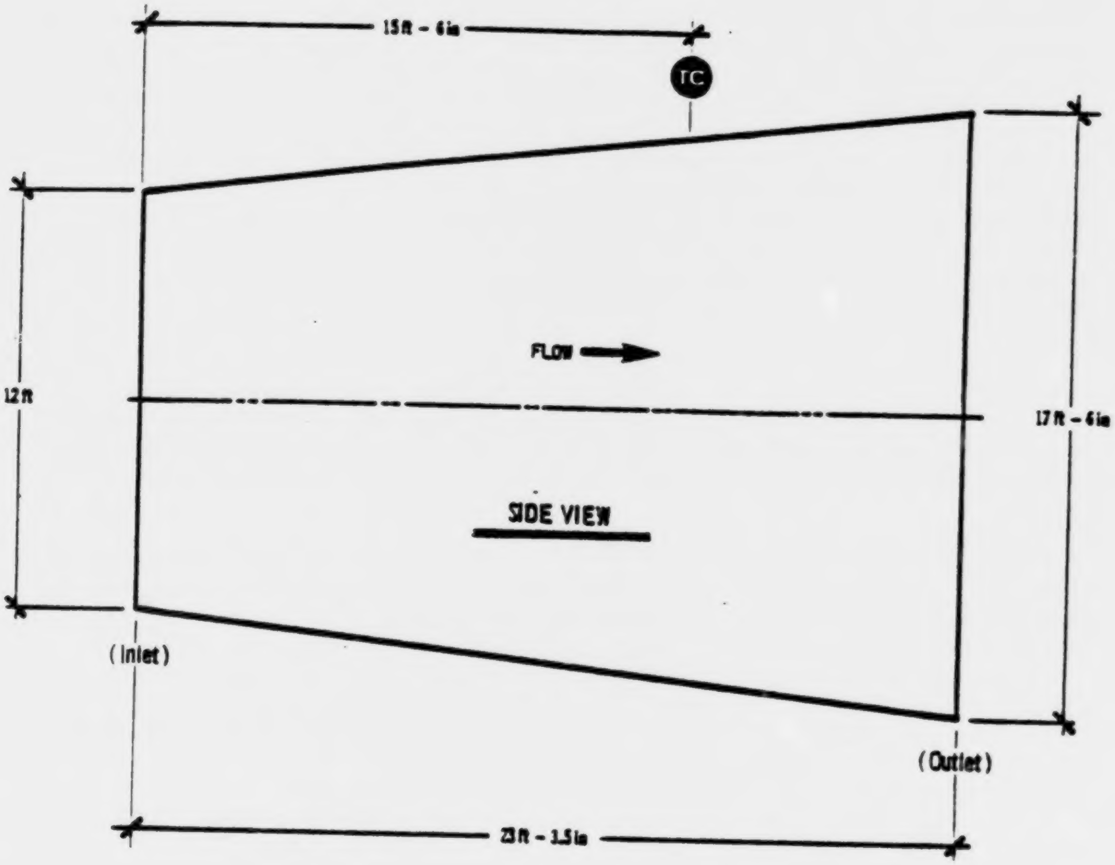
1. Facility and Control Device - The Denka maleic anhydride facility has a nameplate capacity of 23,000 Mg/yr (50 million lbs/yr). The plant was operating at about 70 percent of capacity when the sampling was conducted. The plant personnel did not think that the lower production rate would seriously affect the validity of the results.

Maleic anhydride is produced by vapor-phase catalytic oxidation of benzene. The liquid effluent from the absorber, after undergoing recovery operations, is about 40 weight percent aqueous solution of maleic acid. The absorber vent is directed to the incinerator. The thermal incinerator uses a heat recovery system to generate process steam and uses natural gas as supplemental fuel. The size of the combustion chamber is 2195 ft^2. There are three thermocouples used to sense the flame temperature, and these are averaged to give the temperature recorded in the control room. A rough sketch of the combustion chamber is provided in Figure A-4.

2. Sampling and Analytical Techniques

THC, Benzene, Methane, and Ethane

The gas samples were obtained according to the September 27, 1977, EPA draft benzene method. Seventy-liter aluminized Mylar[R] bags were used with sample times of two to three hours. The sample box and bag were heated to approximately 66°C (150°F) using an electric drum heater and insulation. During Run 1-Inlet, the variac used to control the temperature malfunctioned so the box was not heated for this run. A stainless steel probe was inserted into the single port at the inlet and connected to the gas bag through a tee. The other leg of the tee went to the total organic acid (TOA) train. A Teflon[R] line connected the bag and the tee. A stainless steel probe was connected directly to the bag at the outlet. The lines were


15 ft - 6 in
TC
12 ft
FLOW
SIDE VIEW
17 ft - 6 in
(Inlet)
(Outlet)
23 ft - 1.5 in

There are Three Thermocouples Spaced Evenly Across the Top of the Firebox.

The Width of the Firebox is 6 ft – 6 in.

Figure A–4. Incinerator combustion chamber.

kept as short as possible and not heated. The boxes were transported to the field lab immediately upon completion of sampling. They were heated until the GC analyses were completed.

A Varian model 2440 gas chromatograph with a Carle gas sampling valve, equipped with two cm^3 matched loops, was used for the integrated bag analysis. The SP-1200/Bentone 34 column was operated at 80°C. The instrument has a switching circuit which allows a bypass around the column through a capillary tube for THC response. The response curve was measured daily for benzene (5, 10, and 50 ppm standards) with the column and in the bypass (THC) mode. The THC mode was also calibrated daily with propane (20, 100, and 2000 ppm standards). The calibration plots showed moderate nonlinearity. For sample readings which fell within the range of the calibration standards, an interpolated response factor was used from a smooth curve drawn through the calibration points. For samples above or below the standards, the response factor of the nearest standard was assumed. THC readings used peak height and column readings used area integration measured with an electronic disc integrator.

CO

Analysis for these constituents was done on samples drawn from the integrated gas bag used in THC, benzene, methane, and ethane. Carbon monoxide analysis was done following the GC analyses using EPA Reference Method 10 (Federal Register, Vol. 39, No. 47, March 8, 1974). A Beckman Model 215 NDIR analyzer was used to analyze both the inlet and outlet samples.

Duct Temperature, Pressure, and Velocity

Duct temperature and pressure values were obtained from the existing inlet port. A thermocouple was inserted into the gas sample probe for the temperature while a water manometer was used for the pressure readings. These values were obtained at the conclusion of the sampling period.

Temperature, pressure, and velocity values were obtained for the outlet stack. Temperature values were obtained by thermocouple during the gas sampling. Pressure and velocity measurements were taken according to EPA Reference Method 2 (Federal Register, Vol. 42, No. 160, August 18, 1977). These values also were obtained at the conclusion of the sampling period.

2. Test Results - The Denka incinerator achieves greater than 98 percent reduction at 1400°F and 0.6 second residence time. These results suggest that the recommended 98 percent control level is achievable by properly maintained and operated new incinerators, for which the operating conditions are less stringent than 1600°F and 0.75 second. Table A-1 provides a summary of these test results.

A.1.2.2 Rohm and Haas Test Data[7]

1. Facility and Control Device - The Rohm and Haas plant in Deer Park, Texas, produces acrylic acid and ester. The capacity of this facility has been listed at 400 million lbs/yr of acrylic monomers. Acrylic esters are produced using propylene, air, and alcohols, with acrylic acid produced as an intermediate. Acrylic acid is produced directly from propylene by a vapor-phase catalytic air oxidation process. The reaction product is purified in subsequent refining operations. Excess alcohol is recovered and

heavy end by-products are incinerated. This waste incinerator is designed to burn offgas from the two absorbers. In addition, all process vents (from extractors, vent condensers, and tanks) which might be a potential source of gaseous emissions are collected in a suction vent system and normally sent to the incinerator. An organic liquid stream generated in the process is also burned, thereby providing part of the fuel requirement. The remainder is provided by natural gas. Combustion air is added in an amount to produce six percent oxygen in the effluent. Waste gases are flared during maintenance shutdowns and severe process upsets. The incinerator unit was tested because it operates at relatively shorter residence times (0.75-1.0 seconds) and higher combustion temperatures (1200°-1560°F) than most existing incinerators.

The total installed capital cost of the incinerator was $4.7 million. The estimated operating cost due to supplemental natural gas use is $0.9 million per year.

2. Sampling and Analytical Techniques - Samples were taken simultaneously at a time when propylene oxidations, separations, and esterifications were operating smoothly and the combustion temperature was at a steady state. Adequate time was allowed between the tests conducted at different temperatures for the incinerator to achieve steady state. Bags were used to collect integrated samples and a GC/FID was used for organic analysis.

3. Test Results - VOC destruction efficiency was determined at three different temperatures: 1425°F, 1510°F, and 1545°F. Efficiency is found to increase with temperature and, except for 1425°F, it is above 98 percent. Test results are summarized in Table A-1. These tests were for residence times greater than 0.75 second. However, theoretical calculations show that greater efficiency would be achieved at 1600°F and 0.75 second than at the longer residence times, but lower temperatures represented in these tests.

A.1.2.3 Union Carbide (UCC) Test Data[8]

1. Facility and Control Device - The capacities for the UCC acrylates facilities are about 200 million lbs/yr of acrolein, acrylic acid, and esters. Acrylic acid comprises 130 million lbs/yr of this total. Ethyl acrylate capacity is 90 million lbs/yr. Total heavy ester capacities (such as 2-ethyl-hexyl acrylate) are 110 million lbs/yr. UCC considers butyl acrylate a heavy ester.

The facility was originally built in 1969 and utilized British Petroleum technology for acrylic acid production. In 1976 the plant was converted to a technology obtained under license from Sohio.

The thermal incinerator is one of the two major control devices used in acrylic acid and acrylate ester manufacture. The UCC incinerator was installed in 1975 to destroy acrylic acid and acrolein vapors. This unit was constructed by John Zink Company for an installed cost of $3 million and incorporates a heat recovery unit to produce process steam at 600 psig. The unit operates at a relatively constant feed input and supplements the varying flow and fuel value of the streams fed to it with inversely varying amounts of fuel gas. Energy consumption averages 52.8 million Btu/hr instead of the designed level of 36-51 million Btu/hr. The operating cost in 1976, excluding capital depreciation, was $287,000. The unit is run with nine percent excess oxygen instead of the designed three to five percent excess oxygen. The combustor is designed to handle a maximum of four percent propane in the oxidation feed.

Materials of construction of a non-return block valve in the 600 psig steam line from the boiler section requires that the incinerator be operated at 1200°F instead of the designed 1800°F. The residence time is three to four seconds.

2. Sampling and Analytical Procedures - The integrated gas samples were obtained according to the September 27, 1977, EPA draft benzene method.

Each integrated gas sample was analyzed on a Varian Model 2400 gas chromatograph with FID, and a heated Carle gas sampling valve with matched 2 cm^3 sample loops. A valved capillary bypass is used for total hydrocarbon (THC) analyses and a 2 m, 1/8-in., OD nickel column with PORAPAK® P-S, 80-100 mesh packing is used for component analyses.

Peak area measurements were used for the individual component analyses. A Tandy TRS-80, 48K floppy disc computer interfaced via the integrator pulse output of a Linear Instruments Model 252A recorder acquired, stored, and analyzed the chromatograms.

The integrated gas samples were analyzed for oxygen and carbon dioxide by duplicate Fyrite readings. Carbon monoxide concentrations were obtained using a Beckman Model 215A nondispersive infrared (IR) analyzer using the integrated samples. A three-point calibration (1000, 3000, and 10,000 ppm CO standards) was used with a linear-log curve fit.

Stack traverses for outlet flowrate were made using EPA Methods 1 through 4 (midget impingers) and NO_x was sampled at the outlet using EPA Method 7.

3. Test Results - VOC destruction efficiency was determined at two different temperatures. Table A-1 provides a summary of these test results. Efficiency was found to increase with temperature. At 1475°F, the efficiency was well above 99 percent. These tests were, again, for residence times greater than 0.75 second. However, theoretical calculations show that greater efficiency would be achieved at 1600°F and 0.75 second than at the longer residence times but lower temperatures represented in these tests.

All actual measurements were made as parts per million (ppm) of propane with the other units reported derived from the equivalent values. The values were measured by digital integration.

The incinerator combustion temperature for the first six runs was about 1160°F. Runs 7 through 9 were made at an incinerator temperature of about 1475°F. Only during Run 3 was the acrolein process operating. The higher temperature caused most of the compounds heavier than propane to drop below the detection limit due to the wide range of attenuations used, nearby obscuring peaks, and baseline noise variations. The detection limit ranges from about 10 ppb to 10 ppm, generally increasing during the chromatogram, and especially near large peaks. Several of the minor peaks were difficult to measure. However, the compounds of interest, methane, ethane, ethylene, propane, propylene, acetaldehyde, acetone, acrolein, and acrylic acid, dominate the chromatograms. Only acetic acid was never detected in any sample.

The probable reason for negative destruction efficiencies for several light components is generation by pyrolysis from other components. For instance, the primary pyrolysis products of acrolein are carbon monoxide and ethylene. Except for methane and, to a much lesser extent, ethane and propane, the fuel gas cannot contribute hydrocarbons to the outlet samples.

A sample taken from the inlet line knockout trap showed 6 mg/g of acetaldehyde, 25 mg/g of butenes, and 100 mg/g of acetone when analyzed by gas chromatography/flame ionization detection (GC/FID).

A.1.3 Union Carbide Lab-Scale Test Data[9]

Union Carbide test data show the combustion efficiencies achieved on 15 organic compounds in a lab-scale incinerator operating between 800° and 1500°F and .1 to 2 seconds residence time. The incinerator consisted of a 130 cm, thin bore tube, in a bench-size tube furnace. Outlet analyzers were done by direct routing of the incinerator outlet to a FID and GC. All inlet gases were set at 1000 ppmv.

In order to study the impact of incinerator variables on efficiency, mixing must first be separated from the other parameters. Mixing cannot be measured and, thus, its impact on efficiency cannot be readily separated when studying the impact of other variables. The Union Carbide lab work was chosen since its small size and careful design best assured consistent and proper mixing.

The results of this study are shown in Table A-2. These results show moderate increases in efficiency with temperature, residence time, and type of compound. The results also show the impact of flow regime on efficiency.

Flow regime is important in interpreting the Union Carbide lab unit results. These results are significant since the lab unit was designed for optimum mixing and, thus, the results represent the upper limit of incinerator efficiency. As seen in Table A-2, the Union Carbide results vary by flow regime. Though some large-scale incinerators may achieve good mixing and plug flow, the worst cases will likely require flow patterns similar to complete backmixing. Thus, the results of complete backmixing would be, relatively, more comparable to those obtained from large-scale units.

A.2 NITROGEN OXIDES (NO_x) EMISSIONS

Nitrogen oxides are derived mainly from two sources: (1) from nitrogen contained in the combustion air called thermal NO_x, and (2) from nitrogen chemically combined in the fuel, called fuel NO_x. In addition, combustion of waste gas containing high levels of nitrogen-containing compounds also may cause increases in NO_x emissions. For fuels containing low amounts of nitrogen, such as natural gas and light distillate oils, thermal NO_x is by far the larger component of total NO_x emissions. By contrast, fuel NO_x can account for a significant percentage in the combustion of heavy oils, coal, and other high-nitrogen fuels such as coal-derived fuels and shale oils.

Thermal oxidizer outlet concentrations of NO_x were measured in seven sets of thermal oxidizer tests conducted at three air oxidation plants. Table A-3 provides a summary of the test results. The test results indicate

TABLE A-2. RESULTS OF DESTRUCTION EFFICIENCY UNDER STATED CONDITIONS (UNION CARBIDE TESTS[a])

Flow Regime[b]	Temperature (°F)	Ethyl Acrylate	Residence Time/Compound			
			0.75 second			.5 & 1.5 sec
			Ethanol	Ethylene	Vinyl Chloride	Ethylene
Two-stage Backmixing	1300	99.9	94.6	92.6	78.6	87.2/27.6
	1400	99.9	99.6	99.3	99.0	98.6/99.8
	1500	99.9	99.9	99.9	99.9	99.9/99.9
	1600	99.9	99.9	99.9	99.9	99.9/99.9
Complete Backmixing	1300	98.9	86.8	84.4	69.9	78.2/91.5
	1400	99.7	96.8	95.6	93.1	93.7/97.8
	1500	99.9	99.0	98.7	98.4	98.0/99.0
	1600	99.9	99.7	99.6	99.6	99.4/99.8
Plug Flow	1300	99.9	99.9	99.5	90.2	97.3/99.9
	1400	99.9	99.9	99.9	99.9	99.9/99.9
	1500	99.9	99.9	99.9	99.9	99.9/99.9
	1600	99.9	99.9	99.9	99.9	99.9/99.9

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[a] The results of the Union Carbide work are presented as a series of equations. These equations relate destruction efficiency to temperature, residence time, and flow regime for each of 15 compounds. The efficiencies in this table were calculated from these equations.

[b] Three flow regimes are presented: two-stage backmixing, complete backmixing, and plug flow. Two-stage backmixing is considered a reasonable approximation of actual field units, with complete backmixing and plug flow representing the extremes.

TABLE A-3. SUMMARY OF RESULTS: NO_x DATA

Company	Number of Sets and/or Number of Runs	Outlet NO_x in Flue Gas (ppmv)
Union Carbide	Set 1 (6)	27
	Set 2 (3)	30
Denka	Set 1	9.3
	Set 2	10.2
	Set 3	8.0
Monsanto	Unit 1	200
	Unit 2	8

that NO_x outlet concentrations range from eight to 200 ppmv (0.015 to 0.37 g/m^3). These values could increase by several orders of magnitude in a poorly designed or operated unit. NO_x samples were obtained according to EPA Reference Method 7.

The maximum outlet NO_x concentration of 200 ppmv was measured at an acrylonitrile plant. The vent stream of this plant contains nitrogeneous compounds. The NO_x concentrations measured at the other two plants, whose vent streams do not contain nitrogeneous compounds, range from eight to 30 ppmv (0.015 to 0.056 g/m^3).

A.3 COMPARISON OF TEST RESULTS AND THE TECHNICAL BASIS OF THE SOCMI AIR OXIDATION EMISSIONS LIMIT

This section compares various test results, discusses data and findings on incinerator efficiency, and presents the logic and the technical basis behind the choice of the above control level.

A consideration of VOC combustion kinetics leads to the conclusion that at 1600°F and 0.75 second residence time, mixing is the crucial design parameter. Published literature indicates that any VOC can be oxidized to carbon dioxide and water if held at sufficiently high temperatures in the presence of oxygen for a sufficient time. However, the temperature at which a given level of VOC reduction is achieved is unique for each VOC compound. Kinetic studies indicate that there are two slow or rate-determining steps in the oxidation of a compound. The first is the initial reaction in which the original compound disappears. It has been determined that the initial reaction of methane (CH_4) is slower than that of any other nonhalogenated organic compound. Kinetic calculations show that, at 1600°F, 98 percent of the original methane will react in 0.3 seconds. Therefore, any nonhalogenated VOC will undergo an initial reaction step within this time. After the initial step, extremely rapid free radical reactions occur. Finally, each carbon atom will exist as carbon monoxide (CO) before oxidation is complete. The oxidation of CO is the second slow step. Calculations show that, at 1600°F, 98 percent of an original concentration of CO will react in 0.05 second. Therefore, 98 percent of any VOC would be expected to undergo the initial and final slow reaction steps at 1600°F in about 0.35 second. It is very unlikely that the intermediate free radical reactions would take nearly as long as 0.4 seconds to convert 98 percent of the organic molecules to CO. Therefore, from a theoretical viewpoint, any VOC should undergo complete combustion at 1600°F in 0.75 second. The calculations on which this conclusion is based have taken into account the low mole fractions of VOC and oxygen which would be found in the actual system. They have also provided for the great decrease in concentration per unit volume due to the elevated temperature. But the calculations assume perfect mixing of the offgas and combustion air. Mixing is therefore identified from a theoretical viewpoint as the crucial design parameter.

The test results both indicate an achievable control level of 98 percent at or below 1600°F and illustrate the importance of mixing. Union Carbide results on lab-scale incinerators indicated a minimum of 98.6 percent efficiency at 1400°F. Since lab-scale incinerators primarily differ from field units in their excellent mixing, these results verified the theoretical calculations. The tests cited in Table A-1 are documented as being conducted on full-scale incinerators controlling offgas from air oxidation process vents of a variety of types of plants. To focus on mixing, industrial units were selected where all variables except mixing were held constant or accounted for in other ways. It was then assumed any changes in efficiency would be due to changes in mixing.

The case most directly showing the effect of mixing is that of Petro-tex incinerator. The Petro-tex data show the efficiency changes due to modifications on the incinerator at two times after startup. These modifications included (1) repositioning baffles, (2) adjusting duct slots and openings in the mixing zone to improve exit velocity, (3) installing new dampers, baffles and perforated plates, and (4) rerouting inlet combustion air. These modifications increased efficiency from 70 percent to over 99 percent, with no significant change in temperature.

A comparison indirectly showing the effect of mixing is that of the Rohm and Haas test versus the Union Carbide lab test as presented in Table A-4. These data compare the efficiency of the Rohm and Haas incinerator in combusting four specific compounds with that of the Union Carbide lab unit. The lab unit clearly outperforms the R&H unit. The data from both units are based on the same temperature, residence time, and inlet stream conditions. The more complete mixing of the lab unit is judged the cause of the differing efficiencies. The six tests of in-place incinerators do not, of course, cover every feedstock. However, the theoretical discussion given above indicates that any VOC compound should be sufficiently destroyed at 1600°F. More critical than the type of VOC is the VOC concentration in the offgas. This is true because the kinetics of combustion are not exactly first-order at low VOC concentrations. The Petro-tex results are for a butadiene plant, and butadiene offgas tends to be lean in VOC. Therefore, test results support the validity of the standard for lean streams.

The EPA, Union Carbide, and Rohm and Haas tests were for residence times greater than 0.75 second. However, theoretical calculations show that greater efficiency would be achieved at 1600°F and 0.75 second than at the longer residence times but lower temperatures represented in these two tests. The data on which the standard is based are test data for similar control systems: thermal incineration at various residence times and temperatures. If 98 percent VOC reduction can be achieved at a lower temperature, then according to kinetic theory it can certainly be achieved at 1600°F, other conditions being equal.

Four tests at temperatures less than 1600°F are relied upon to support the 98 percent reduction requirement.

TABLE A-4. RESULT COMPARISONS OF LAB INCINERATOR vs. ROHM & HAAS INCINERATOR[a]

Compound	Rohm & Haas Incinerator Inlet (lbs/hr)	Rohm & Haas Incinerator Outlet (lbs/hr)	Union Carbide Lab Incinerator Inlet (lbs/hr)	Union Carbide Lab Incinerator Outlet (lbs/hr)
Propane	900	150	71.4	0.64
Propylene	1800[b]	150[b]	142.9	5.6
Ethane	10	375	0.8	3.9
Ethylene	30	190	2.4	3.4
TOTAL	2740	865	217.5	13.54
% VOC Destruction:	68.4%		93.8%	

[a] Table shows the destruction efficiency of the four listed compounds for the Rohm & Haas (R&H) field and Union Carbide (UC) lab incinerators. The R&H results are measured; the UC results are calculated. Both sets of results are based on 1425°F combustion temperature and one second residence time. In addition, the UC results are based on complete backmixing and a four-step combustion sequence consisting of propane to propylene to ethane to ethylene to CO_2 and H_2O. These last two items are worst case assumptions.

[b] Are not actual values. Actual values are confidential. Calculations with actual values give similar results.

A.4 REFERENCES FOR APPENDIX A

1. Mascone, D.C., EPA, Draft memorandum concerning incinerator efficiency, April 25, 1980.

2. Letter from Towe, R., Petro-Tex Chemical Corporation, to Farmer, J., EPA, August 15, 1979.

3. Broz, L.D. and Pruessner, R.D., "Hydrocarbon Emission Reduction Systems Utilized By Petro-Tex," paper presented at 83rd National Meeting of AIChE, 9th Petrochemical and Refining Exposition, Houston, Texas, March 1977.

4. Letter from Lawrence, A., Koppers Company, Inc., to Goodwin, D., EPA, January 17, 1979.

5. Letter from Weishaar, M., Monsanto Chemical Intermediates Co., to Farmer, J., EPA, November 8, 1979.

6. Maxwell, W., and Scheil, G., "Stationary Source Testing Of A Maleic Anhydride Plant At The Denka Chemical Corporation, Houston, Texas," EPA Contract No. 68-02-2814, March, 1978.

7. Blackburn, J., Emission Control Options For The Synthetic Organic Chemicals Manufacturing Industry, Trip Report, EPA Contract No. 68-02-2577, November 1977.

8. Scheil, G., Emission Control Options for The Synthetic Organic Chemicals Manufacturing Idustry, Trip report, EPA Contract No. 68-02-2577, November 1977.

9. Lee, K., Hansen, J., and Macauley, D.," Thermal Oxidation Kinetics Of Selected Organic Compounds," paper presented at the 71st Annual Meeting of the APCA, Houston, Texas, June 1978.

APPENDIX B: STATISTICAL ANALYSIS

APPENDIX B: STATISTICAL ANALYSIS

B.1 INTRODUCTION

The purpose of this appendix is to describe the methods of statistical analysis used in the development of the control techniques guideline (CTG) document for the air oxidation unit process segment of SOCMI. The method of regulatory analysis developed for this CTG uses a national statistical profile, representing the air oxidation segment of SOCMI to project the energy, cost, and environmental impacts associated with VOC control using reasonably available control technology (RACT).

B.2 STATISTICAL IMPACT ANALYSIS

Typically, a CTG would be developed on a chemical-by-chemical basis. Because the processes used by a single chemical-producing industry to manufacture a specific product do not differ greatly, it is possible to design a model plant that can be used to represent the emissions and control device requirements of typical existing sources covered in the CTG. This model, along with knowledge of the existing population of sources, would be used to determine the environmental, energy, and cost impacts associated with RACT.

Air oxidation facilities, however, use 36 types of oxidation processes (23 principal processes and 13 specialty processes) to manufacture 36 different organic chemicals. Because of the number and diversity of facilities and processes in the air oxidation industry, a chemical-by-chemical development of CTG's would require large amounts of time, effort, and money. The unit process approach, on the other hand, allows development of a CTG that provides for RACT development for VOC emissions from all SOCMI air oxidation processes. This unit process approach allows the resource-efficient statistical estimation of the RACT impacts for VOC emissions control from all air oxidation processes.

In the unit process approach, no model plants are used for impact analysis. Rather, the information concerning existing air oxidation facilities is analyzed statistically and used to construct a national profile. This national profile replaces the traditional model plant and can be considered a statistical model of SOCMI air oxidation processes and facilities. The national profile characterizes air oxidation processes according to national distributions of key variables (e.g., waste gas stream flow, heating value, and VOC content) that can be used to determine VOC emissions and the cost and energy impacts associated with RACT. RACT is therefore recommended as a percent VOC emission reduction based on thermal oxidation as the single control technique. The RACT impacts are evaluated as impacts upon the entire population of affected facilities.

B.2.1 National Statistical Profile Construction

The overall success of the statistical analysis depends on the availability of an adequate sample size and dependable data. Thirty-six chemicals are produced by air oxidation processes nationwide. The results of the EPA Houdry Questionnaires contain data on 13 chemicals. These data consist of emission and production factors for 59 chemical plants, representing 36 percent of the total population. These results, along with the physical properties of the chemicals involved, form the basis of the analysis. Table B-1 lists the chemicals that are included in the data base.

As noted, the data base for CTG analysis has been derived from EPA Houdry Questionnaires. The Houdry Division of Air Products and Chemicals, Inc., conducted an extensive survey of the petrochemical industry to provide data for EPA to use in their fulfillment of their obligations under the terms of the Clean Air Amendments of 1970. The scope of that study included most petrochemicals which fell into one or more of the classifications of (1) large production, (2) high growth rate, and (3) significant air pollution. The information sought included industry descriptions, air emission control problems, sources of air emissions, statistics on quantities and types of emissions, and descriptions of emission control devices then in use. The principal source for that data was the industry questionnaire current as of 1972. The data base was updated in 1979.

Table B-2 shows the actual data base used to construct the national statistical profile. Twenty-three different processes are represented in the data set. Due to the wide variation in processes used and in the types of control devices present across the air oxidation industry, only uncontrolled emission factors and vent stream characteristics are included in the data set. Since uncontrolled emissions are subject to the greatest uncertainty because of the difficulty in defining what is a pollution control device, all stream data represent the process stream exiting the primary product recovery device. Figure B-1 shows the reference point for data collection within the air oxidation process. Since many air oxidation facilities may have additional control equipment in place, these data are overstated estimates of the current emission factors. Table B-3 shows the air oxidation offgas components specific to each chemical represented in the data base. Table B-4 shows the data vectors contained in the national statistical profile. Tables B-5 and B-6 show tabular representations of the vector distribution.

B.2.2 Data Reliability

From the Houdry data, two assumptions must be made regarding the Houdry data reliability for this CTG analysis. First, the data contain a bias toward large-volume chemicals or those chemicals with significant air pollution. This is not considered to be a serious drawback to the CTG analysis. Second, because the chemical industry as a whole is dynamic, the age of the Houdry data presented a second source of bias. In a study prepared for the Chemical Manufacturers Association (CMA), the 1972 Houdry data (updated in 1979) were compared to a 1980 data base developed from recent industry contacts. Twenty-two plants are represented in both the CMA data base and the data base used for this CTG analysis. Emission factors were calculated for each data vector representing a plant for which data exist in both data bases. Two sets of 22 emission factors each, one set for each data base, were thereby obtained. These two sets were statistically compared using the Wilcoxon signed-rank procedure. The results of the Wilcoxon signed-rank procedure to test the significance of the differences between the overlapping portions of the two data bases show that the differences are not significant at the 0.05 level.

TABLE B-1. LIST OF CHEMICALS FOR WHICH DATA HAVE BEEN OBTAINED

- Ethylene Oxide
- Hydrogen Cyanide
- Acetic Acid
- Acetaldehyde
- Phthalic Anhydride
- Dimethyl Terephthalate
- Phenol
- Ethylene Dichloride
- Acrylonitrile
- Cyclohexanone
- Terephthalic Acid
- Maleic Anhydride
- Formaldehyde

TABLE B-2. ACTUAL DATA BASE USED TO CONSTRUCT NATIONAL STATISTICAL PROFILE

Company	Location	Process
Rohm & Haas	Deer Park, TX	Methane/Ammonia Oxidation
Badische	Freeport, TX	Cyclohexane Oxidation
Badische	Freeport, TX	Cyclohexane Oxidation
Nipro	Augusta, GA	Cyclohexane Oxidation
Clark	Blue Island, IL	Cumene Hydroperoxidation
Dow	Oyster Creek, TX	Cumene Hydroperoxidation
Georgia Pacific	Plaquemine, LA	Cumene Hydroperoxidation
Monsanto	Choc. Bayou, TX	Cumene Hydroperoxidation
Shell	Deer Park, TX	Cumene Hydroperoxidation
USS	Haverhill, OH	Cumene Hydroperoxidation
DuPont	Wilmington, NC	DMT p-Xylene Oxidation
DuPont	Old Hickory, TN	DMT p-Xylene Oxidation
Eastman	Kingsport, TN	TPA p-Xylene Oxidation
Amoco/Standard	Decatur, AL	TPA p-Xylene Oxidation
Exxon	Baton Rouge, LA	o-Xylene Oxidation
Monsanto	Texas City, TX	o-Xylene Oxidation
Stepan	Millsdale, IL	o-Xylene Oxidation
Conoco	Covenant, LA	Ethylene Oxychlorination
Diamond Shamrock	Deer Park, TX	Ethylene Oxychlorination
Dow	Freeport, TX	Ethylene Oxychlorination
Ethyl	Baton Rouge, LA	Ethylene Oxychlorination
Goodrich	Calvert City, KY	Ethylene Oxychlorination
ICI	Baton Rouge, LA	Ethylene Oxychlorination
Shell	Deer Park, TX	Ethylene Oxychlorination
Stauffer	Long Beach, CA	Ethylene Oxychlorination
Vulcan	Grismar, LA	Ethylene Oxychlorination
Dow	Freeport, TX	Ethylene Oxidation I
Koch	Orange, TX	Ethylene Oxidation I
UCC	Seadrift, TX	Ethylene Oxidation I
PPG	Beaumont, TX	Ethylene Oxidation I
Eastman	Longview, TX	Ethylene Oxidation II
American Cyanamid	New Orleans, LA	Propylene Ammoxidation
DuPont	Beaumont, TX	Propylene Ammoxidation
Monsanto	Alvin, TX	Propylene Ammoxidation
Vistron	Lima, OH	Propylene Ammoxidation
Denka	Houston, TX	Benzene Oxidation
Monsanto	St. Louis, MO	Benzene Oxidation
Koppers	Bridgeville, PA	Benzene Oxidation
Reichhold	Morris, IL	Benzene Oxidation
Reichhold	Elizabeth, NJ	Benzene Oxidation

TABLE B-2 (Concluded). ACTUAL DATA BASE USED TO CONSTRUCT NATIONAL STATISTICAL PROFILE

Company	Location	Process
Tenneco	Fords, NJ	Benzene Oxidation
USS	Neville Island, PA	Benzene Oxidation
USS	Neville Island, PA	Naphthalene Oxidation
UCC	Charleston, WV	Naphthalene Oxidation
Gulf	Vicksburg, MS	Methanol Oxidation I
Reichhold	Houston, TX	Methanol Oxidation I
GAF	Calvert City, KY	Methanol Oxidation I
Reichhold	Moncure, NC	Methanol Oxidation I
Borden	Fayetteville, NC	Methanol Oxidation II
Celanese	Bishop, TX	Methanol Oxidation II
DuPont	Belle, WV	Methanol Oxidation II
Georgia Pacific	Vienna, GA	Methanol Oxidation II
Monsanto	Choc. Bayou, TX	Methanol Oxidation II
Georgia Pacific	Crossett, AR	Methanol Oxidation II
Hercules	Wilmington, NC	Methanol Oxidation II
Reichhold	Kansas City, KS	Methanol Oxidation II
Tenneco	Garfield, NJ	Methanol Oxidation II
Eastman	Kingsport, TN	Acetaldehyde Oxidation

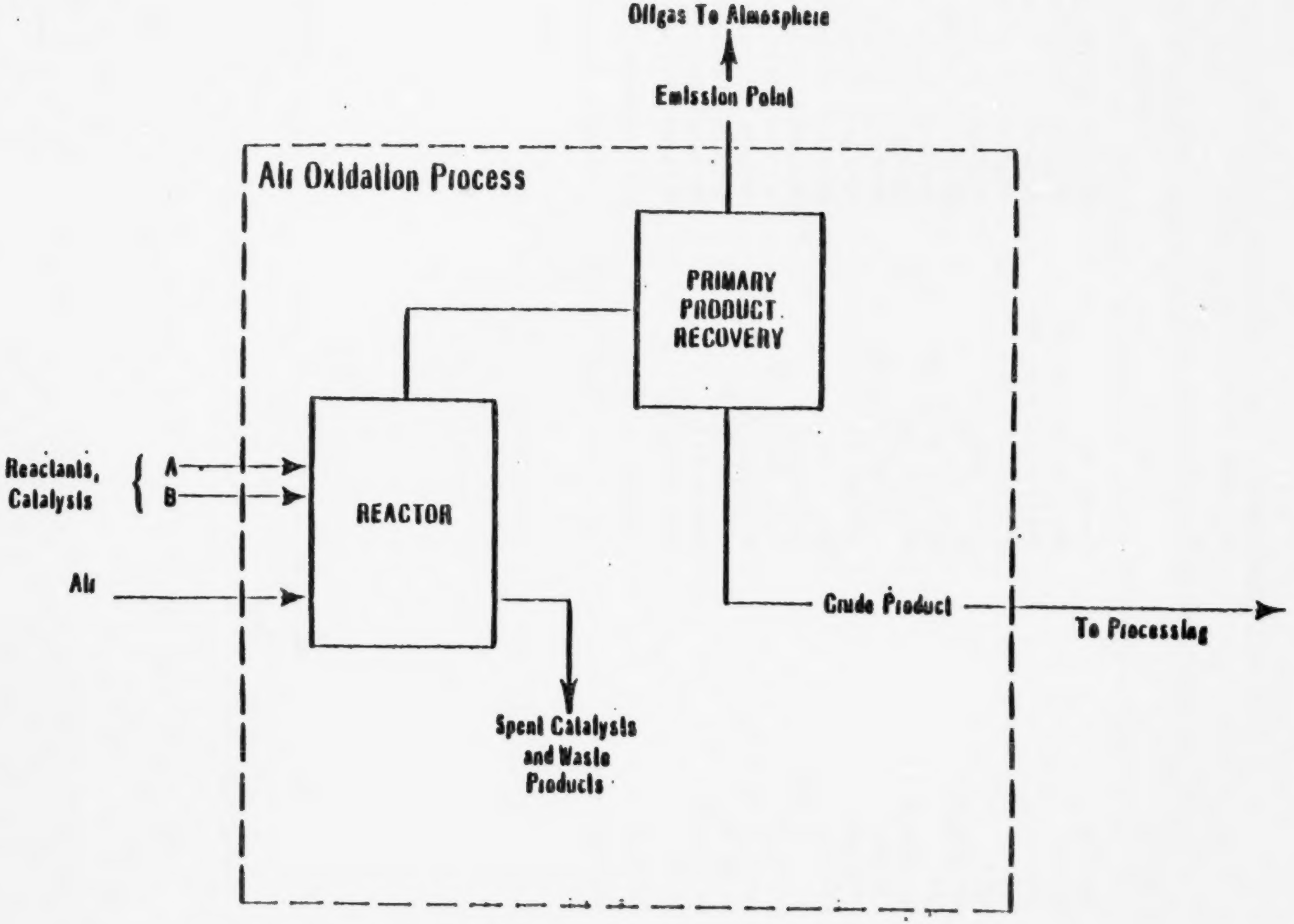
Offgas To Atmosphere
Emission Point
Air Oxidation Process
PRIMARY PRODUCT RECOVERY
Reactants, Catalysis
A
B
REACTOR
Air
Crude Product
To Processing
Spent Catalysis and Waste Products

Figure B-1. General Air-Oxidation Process.

TABLE B-3. AIR OXIDATION OFFGAS COMPONENTS

ACRYLONITRILE

Nitrogen
Oxygen
Carbon Dioxide
Carbon Monoxide
Water (vapor)
Ammonia*
Methane
Ethane
Ethylene
Propane
Propylene*
Acetaldehyde
Acetone (vapor)
Acrolein (propenal) (vapor)
Hydrogen Cyanide
Acrylonitrile (vapor)*
Acetonitrile (vapor)

HYDROGEN CYANIDE

"Air"
Hydrogen Cyanide*

ACETIC ACID

Nitrogen
Oxygen
Carbon Dioxide
Water (vapor)
Carbon Monoxide*

CYCLOHEXANONE

Nitrogen
Carbon Monoxide
Cyclohexane (vapor)*
Cyclohexanol (vapor)
Cyclohexanone (vapor)*
"Unknown Organics (C_2^+)"

ACETALDEHYDE

Nitrogen
Oxygen
Carbon Dioxide
Carbon Monoxide
Water (vapor)
Hydrogen
Methane
Methyl Chloride
Ethyl Chloride
Ethanol (vapor)*
Acetic Acid (vapor)
Acetaldehyde (vapor)*
Argon

ACETIC ANHYDRIDE

Nitrogen
Oxygen
Carbon Dioxide
Carbon Monoxide
Hydrogen

TABLE B-3 (Continued). AIR OXIDATION OFFGAS COMPONENTS

- Argon
- Hydrogen
- Methane
- Ethane
- Butane*
- "C_2^+ Hydrocarbons"
- Methyl Iodide
- Ethanol*
- Acetaldehyde*
- Methyl Acetate
- Ethyl Acetate
- Methane
- Ethane
- Ethylene
- Propane
- Propadiene
- Acetic Acid (vapor)*
- Diketene (vapor) "$(CH_2=C=O)_2$"
- Acetic Anhydride (vapor)*

MALEIC ANHYDRIDE

- Nitrogen
- Oxygen
- Carbon Dioxide
- Water (vapor)
- Carbon Monoxide
- Formaldehyde
- Formic Acid (vapor)
- Maleic Acid (vapor)
- Maleic Anhydride (vapor*)
- Benzene (vapor)*
- Xylene (vapor)
- "Other Organics (Est. Mol. Wt. 50)"

PHTHALIC ANHYDRIDE

- Nitrogen
- Oxygen
- Water (vapor)
- Carbon Monoxide

PHENOL

- Nitrogen
- Oxygen
- Water (vapor)
- Carbon Dioxide

TABLE B-3 (Continued). AIR OXIDATION OFFGAS COMPONENTS

PHTHALIC ANHYDRIDE

Carbon Dioxide
Argon
Sulfur Dioxide*
Inorganic Salts (Magnesium and Calcium Carbonates) (particulate)
"Hydrocarbons"
Maleic Acid (vapor)
Maleic Anhydride (vapor)
Benzoic Acid (vapor)
Phthalic Anhydride*
1,2-Naphthoquinone (particulate, vapor)

PHENOL

Sodium Carbonate (particulate)
Formaldehyde
Acetaldehyde
Acetone (vapor)
Acetone (vapor)
Mesityl Oxide (4-Methyl-3-Penten-2-One) (vapor)
Benzene (vapor)
Phenol (vapor)*
Cumene (vapor)*
Cumene Hydroperoxide (vapor)
a-Methyl Styrene (vapor)
a,a-Dimethyl Benzyl Alcohol (2-Phenyl-2-Propanol) (vapor)
Acetophenone
Other Organics", "Oxidized Organics (various)" (vapor)

TEREPHTHALIC ACID & DIMETHYL TEREPHTHALATE

Nitrogen
Oxygen
Water (vapor)
Carbon Dioxide
Carbon Monoxide
Methane
Methanol*
Dimethyl Ether
Methyl Ethyl Ketone (vapor)*

ETHYLENE OXIDE

Nitrogen
Oxygen
Carbon Dioxide
"Oxides of Nitrogen"

TABLE B-3 (Concluded). AIR OXIDATION OFFGAS COMPONENTS

TEREPHTHALIC ACID & DIMETHYL TEREPHTHALATE	ETHYLENE OXIDE
Methyl Acetate (vapor)	Argon
Acetic Acid (vapor)*	Methane
Acetaldehyde*	Ethane
p-Xylene (vapor)*	Ethylene*
	Ethylene Oxide*
	"Particulate (Primarily Carbon, small amounts of Iron, Chlorine)

---

*Product or Feedstock

TABLE B-4. DISTRIBUTION OF NATIONAL STATISTICAL PROFILE DATA VECTORS

Plant ID Number	Hourly Emissions (kg/hr)	Net Heating Value (MJ/Nm^3)	Offgas Flowrate (Nm^3/min)
1303	326	0.635	430
1305	666	1.13	493
1306	115	0.535	181
1307	2.12	0.001	2830
1601	55.0	3.55	1520
205	75.0	0.251	142
2301	117	0.150	736
2302	203	0.154	1130
2303	617	0.099	3310
2305	340	0.097	2150
2308	219	0.157	1230
5101	1370	1.12	1330
5102	2150	1.71	1280
5103	895	0.781	1420
5104	1210	0.725	1950
102	13.7	0.010	340
1004	323	0.289	1420
1007	223	0.165	527
2203	155	0.233	481
2204	26.4	0.067	425
2205	27.9	0.070	289
2206	36.0	0.093	215
2207	13.7	0.070	142
2208	14.6	0.117	90.6
902	80.2	0.472	170
903	103	0.465	170
904	407	1.63	235
1001	78.7	0.393	1530
1005	188	0.153	912
1801	529	0.419	2110
1802	211	0.360	1250
1803	205	0.415	1190
1804	136	0.483	481
1805	14.1	0.220	1220
1806	135	0.359	850
1807	355	0.808	566
1403	15.1	2.82	22.7
1404	20.3	2.63	67.9
1407	33.7	2.82	56.6
1408	14.6	2.72	70.8
1409	0.0250	2.95	31.1
1410	15.8	2.71	161
1411	357	3.05	510
1418	0.0205	2.56	25.5
1416	39.6	0.114	164
1421	16.0	0.148	110
1423	19.5	0.148	110
1422	23.3	0.321	93.4
1420	31.4	2.76	56.6
1601	0.217	1.83	184
5202	80.2	0.807	170
5203	433	2.13	113
5204	348	2.84	201
5205	228	2.15	603
5206	125	0.775	133
5207	464	0.825	283
5208	371	0.825	226
5209	78.9	0.825	48.1
5201	616	4.56	259

TABLE B-5. JOINT DISTRIBUTION OF FLOW AND MASS EMISSIONS IN NATIONAL STATISTICAL PROFILE

Offgas Flow (W) Nm^3/min	Hourly Emissions (E) kg/hr					
	$E \le 5$	$5 < E \le 25$	$25 < E \le 50$	$50 < E \le 100$	$100 < E \le 200$	$200 < E$
$W \le 14$	-	-	-	-	-	-
$14 < W \le 28$	1	1	3	-	-	-
$28 < W \le 142$	1	9	2	-	1	1
$142 < W \le 708$	1	7	3	3	7	1
$708 < W \le 1420$	-	1	-	6	1	3
$1420 < W$	1	1	1	-	1	3

TABLE B-6. JOINT DISTRIBUTION OF DESIGN CATEGORIES AND MASS EMISSIONS IN NATIONAL STATISTICAL PROFILE

Category	Net Heating Value (H_T) MJ/Nm^3	Hourly Emissions (E) kg/hr					
		$E \leq 5$	$5 < E \leq 25$	$25 < E \leq 50$	$50 < E \leq 100$	$100 < E \leq 200$	$200 < E$
A1 (Halogenated)	$0 \leq H_T \leq 3.5$	-	-	3	-	3	1
A2 (Halogenated)	$3.5 < H_T$	-	-	-	-	-	-
B (Not Halogenated)	$0 \leq H_T \leq 0.48$	1	12	6	7	4	6
C (Not Halogenated)	$0.48 \leq H_T \leq 1.9$	3	7	-	2	3	1
D (Not Halogenated)	$1.9 \leq H_T \leq 3.6$	-	-	-	-	-	-
E (Not Halogenated)	$3.6 < H_T$	-	-	-	-	-	-

B.2.3 National Statistical Profile Use

The actual use of the national statistical profile assumes that the distribution of offgas flow, mass emissions, and stream heating value is chemical independent. Chemical identities are not considered in the profile, nor is there claimed to be a one-to-one correspondence between any one data vector and an existing offgas stream. It is assumed, however, that the overall proportions and distributions of the parameter values and data vectors are similar to those of the existing population of air oxidation facilities. Thus, since the national statistical profile contains 59 data vectors, each data vector and associated impacts of pollution control represents 1/59 of the existing population to be analyzed for control.

B.2.4 Calculation of Baseline Control Level[1]

As mentioned earlier, the data base was constructed from uncontrolled emission sources. However, some control is currently being applied to the sources as required by current State Implementation Plans (SIP's) or other regulations. In order to modify the collection of data vectors to account for existing control, an analysis of the SIP requirements and an adjustment of the profile is required.

A weighted average of current control requirements appears to provide the closest approximation of current VOC control levels. The baseline analysis assumes that the statistical profile of data vectors adequately represents the population of existing air oxidation processes within each State. An annual emission value was calculated for each data vector from its hourly emission value. These values were summed to give a total annual emission value for the profile. Each data vector was analyzed in order to estimate whether a plant with such offgas characteristics would be required to reduce VOC emissions by a given SIP. For each data vector determined to be subject to SIP control, the annual emission reduction under SIP was calculated. The total annual emission reduction associated with the given SIP was calculated as the sum of these individual vector values. This emission reduction value was divided by the total emission value for the profile. The result was an estimated percent reduction of emissions for a given State. The national baseline was then calculated as a weighted average of the baselines for each State. In calculating the national weighted average, each individual State baseline control value was weighted by the estimated percent of nationwide nonattainment area emissions from nonattainment areas located within the respective State. For each existing facility located in a nonattainment area, the plant capacity was multiplied by the appropriate emission factor from Appendix D. The resulting plant emission estimates were summed according to State, and percentages calculated for each State to give the weighting factors. Analysis shows that the estimated baseline control level attributable to the existing SIP's is 58 percent. Consequently, a 58 percent VOC reduction from the uncontrolled level is used as the baseline level for analysis of the RACT impacts.

B.3 REFERENCES FOR APPENDIX B

1. Memo from Galloway, J., EEA, to SOCMI Air Oxidation File. July 29, 1981. Calculation of baseline emissions.

APPENDIX C: EMISSION FACTORS

APPENDIX C: EMISSION FACTORS

The following emission factors and sample calculations are included to form a basis for the verification of VOC emission inventories developed from emission source tests, plant site visits, permit applications, etc. These factors and procedures should not be applied in cases where site-specific data are available, but rather in instances where specific plant information is lacking or highly suspect.

C.1 VOC EMISSION FACTORS FOR EXISTING EQUIPMENT

Table C-1 contains selected emission factors for each SOCMI air oxidation chemical process being considered.[1] To provide uniformity across the various processes and to account for the differences in vent streams inherent among the processes, a general emission point common to all processes was selected.

Several criteria were used when selecting the point or points in any given process at which VOC emissions data would be gathered and incorporated into development of the emission factor. The data were generated primarily from the point at which the bulk of the N_2 from the air used in the reaction was vented to the atmosphere. The relevant point was prior to any combustion device and downstream from any other product recovery or emission control device.

Typical annual VOC emissions for four selected processes employing existing and reasonably available control technology (RACT) equipment are given in Table C-2.

C.2 PRECAUTIONS TO BE CONSIDERED WHEN UTILIZING EMISSION FACTORS

C.2.1 Extreme Range of Some Emission Factors

In some cases, plants using a given process reported widely differing emission factors. Such extreme ranges indicate emission variability inherent to a process and/or inaccurate data. Emission estimations derived from an average of such a range of emission factors may differ significantly from the actual emissions of any given plant.

C.2.2 Cost-Effectiveness Cutoff with Respect to RACT Equipment

RACT would not involve reduction of the vent stream VOC concentration by 98 percent or to 20 ppm if the total resource effectiveness (TRE) index value (described in Appendix E) of the process vent stream is above 1.0. The selection of this level was based on the overall resource use required to destroy a unit amount of process vent stream VOC using thermal oxidation. All resources which are expected to be used in VOC control by thermal oxidation are taken into account. The primary resources used are capital and supplementary energy. The total resource effectiveness index is derived and specifically defined in Chapter 5, "Cost Analysis." The TRE index value of a facility is based on the characteristics of the offgas from the final piece of product recovery equipment. Therefore, the use of a cutoff TRE index level is meant to encourage the use of product recovery techniques or process modifications to reduce emissions. A plant could add product

TABLE C-1. VOC EMISSION FACTORS FOR SOCMI CHEMICALS (AIR OXIDATION PROCESSES)[1]

Chemical (Process)	Number of Data Points Considered	Emission Factor ($\frac{\text{kg VOC Emitted}}{\text{Mg Product}}$) Range	Selected Value
Acetaldehyde (Wacker)	2	0.6 to 2.3	1.4
Acetaldehyde (ethanol)	1	Only one reported value	.02
Acetic Acid (Wacker)	4	7 to 16	11
Acetic Acid (butane)	1	Only one reported value	7.0
Acetone (Hercules cumene)	3	2 to 6	3.7
Acetone (Allied cumene)	5	3 to 20	10
Acrylic Acid	3	90 to 200	120
Acrylonitrile (Propene ammoxidation)	6	98 to 210	110
Anthraquinone	0	Insufficient information available	
Benzaldehyde	0	Insufficient information available	
Benzoic Acid	1	Only one reported value	2.0
1,3-Butadiene	2	1.7 to 5	3.3
p-t-Butyl Benzoic Acid	0	Insufficient information available	
n-Butyric Acid	1	Only one reported value	.5
Crotonic Acid	0	Insufficient information available	
Cyclohexanol	5	10 to 52	38
Dimethyl Terephthalate/Terephthalic Acid	6	2.4 to 15	10
Ethylene Dichloride	11	6 to 36	12
Ethylene Oxide	6	33 to 79[a]	48
Formaldehyde (metal oxide)	6	3 to 34	8
Formaldehyde (silver catalyst)	11	3 to 22[b]	6.5
Glyoxal	0	Insufficient information available	
Hydrogen Cyanide	2	6 to 8	7
Isobutyric Acid	1	Only one reported value	55
Isophthalic Acid	2	2 to 19	11
Maleic Anhydride (benzene)	9	12 to 230	93
Maleic Anhydride (butane)	1	Only one reported value	19
Phthalic Anhydride (xylene)	3	76 to 92	85
Phthalic Anhydride (naphthalene)	2	25 to 34	30
Propionic Acid (propionaldehyde)	1	Only one reported value	6
Propylene Oxide (ethylbenzene)	3	.2 to .7	.5

[a] One stream with reported VOC precent below detection limits not incorporated in range.

[b] Two streams with reported VOC percent below detection limits not incorporated in range.

TABLE C-2. TYPICAL ANNUAL VOC EMISSIONS FOR FOUR SELECTED PROCESSES EMPLOYING EXISTING AND RACT EQUIPMENT

Type of Plant	Plant Production Gg/yr (mm lb/yr)	Emission Factor in kg VOC Emitted/Mg Product		Average VOC Emissions in Gg/yr (lb/yr)		Annual VOC Emission Reductions Resulting from RACT Implementation in Gg/yr (lb/yr)
		Existing Equipment	RACT Equipment	Existing Equipment	RACT Equipment	
Small Formaldehyde	16 (36)	6.5	0.13	0.10 (2.3×10^5)	2.1×10^{-3} (4.6×10^3)	0.10 (2.3×10^5)
Large Formaldehyde	144 (318)	6.5	0.13	0.95 (2.1×10^6)	1.9×10^{-2} (4.1×10^4)	0.95 (2.1×10^6)
Small Ethylene Dichloride	45.4 (100)	12	0.24	0.54 (1.2×10^6)	1.1×10^{-2} (2.4×10^4)	0.54 (1.2×10^6)
Large Ethylene Dichloride	300 (660)	12	0.24	3.6 (7.9×10^6)	7.3×10^{-2} (1.6×10^5)	3.5 (7.7×10^6)

recovery equipment, and thereby be transferred to the RACT category of no further control, by exceeding the TRE cutoff. It is therefore erroneous to assume that RACT equipment will reduce by 98 percent VOC emissions in all plants affected by the CTG.

C.3 VOC EMISSION FACTORS AS APPLIED TO EXAMPLE PROCESSES

C.3.1 Sample Calculation, Hydrogen Cyanide Plant

C.3.1.1 Existing Equipment

$$\frac{\text{Existing Equipment}}{\text{Emission Factor (kg/Mg)}} \times \frac{\text{Gg Product}}{\text{Produced/yr}} = \frac{\text{Mg VOC Emitted/yr by}}{\text{Existing Equipment}}$$

(7) x (52.6 Gg/yr) = 368 Mg VOC Emitted by Existing Equipment/yr

C.3.1.2 RACT Equipment

(Existing Equipment Emission Factor (kg/Mg)) x Weight % VOC Emissions Expected to Remain After RACT Equipment = RACT Equipment Emission Factor (kg/Mg)

(7) x (.02) = .14

RACT Equipment Emission Factor (kg/Mg) x Gg Product Produced/yr = Mg VOC Emitted/yr by RACT Equipment

(.14) x (52.6 Gg/yr) = 7.36 Mg VOC Emitted/yr by RACT Equipment

C.3.2 Plant VOC Emission Reduction Efficiency, Hydrogen Cyanide Plant

C.3.2.1 Total Annual Plant VOC Emission Reduction

Total Annual Emissions from Existing Equipment − Total Annual Emissions from RACT Equipment = Total Annual Emission Reduction

368 Mg VOC/yr - 7.36 Mg VOC/yr = 361 Mg VOC/yr

C.3.2.2 Percent Reduction in Total Plant VOC Emissions

Total Annual Emission Reduction ÷ Total Annual Emissions from Existing Equipment = % Reduction in Total Plant VOC Emissions

(361 Mg VOC/yr) ÷ (368 Mg VOC/yr) = 98% Reduction in Total Plant VOC Emissions

C.4 REFERENCES FOR APPENDIX C

1. Memo from Galloway, J., EEA, to SOCMI Air Oxidation File. July 29, 1981. Calculation of baseline emissions level.

APPENDIX D: RACT CALCULATIONS

APPENDIX D: RACT CALCULATIONS

D.1 INTRODUCTION

This appendix presents calculations and derivations related to the definition and implementation of the recommended RACT (from this point on the recommended RACT is simply referred to as RACT).

D.2 TOTAL RESOURCE EFFECTIVENESS

RACT is based on incineration of certain process vent streams discharged to the atmosphere. The streams for which RACT involves this VOC reduction are those for which the associated total resource effectiveness (TRE) index value is less than 1.0. Thermal oxidation can reduce VOC emissions by 98 weight percent or to 20 ppm (volume, by compound), whichever is less stringent. An index value of TRE can be associated with each air oxidation vent stream for which the offgas characteristics of flowrate, hourly emissions and net heating value are known. For facilities with a process vent stream or combination of process vent streams having a TRE index value which exceeds the cutoff level of 1.0, the removal of VOC using thermal incineration is not required.

TRE is a measure of the supplemental total resource requirement per unit VOC reduction, associated with VOC control by thermal oxidation. All resources which are expected to be used in VOC control by thermal oxidation are taken into account in the TRE index. The primary resources used are supplemental natural gas, capital, and (for offgas containing halogenated compounds) caustic. Other resources used include labor, electricity, and (for offgas containing halogenated compounds) scrubbing and quench makeup water.

The TRE index is derived from the cost effectiveness associated with VOC control by thermal oxidation. The calculation of cost effectiveness and derivation of the TRE index are given in detail in Chapter 5. The TRE index of a vent stream is defined as the cost-effectiveness value of the stream, divided by a cost-effectiveness value of $1,600/Mg. The TRE index is a convenient, dimensionless measure of the total resource burden associated with VOC control at a facility. It is independent of the general inflation rate. However, it does assume fixed relative costs of the various resources, such as carbon steel and electricity.

States may choose to establish a cost-effectiveness cutoff different from the \$1,600/Mg cutoff recommended in this CTG. Even if a State were to establish a different cost-effectiveness cutoff, the existing TRE equation and coefficients could still be used provided that a correction factor is applied. The correction factor would be equal to the existing TRE index multiplied by \$1,600/Mg and divided by the desired cost-effectiveness cutoff.

The distinction in RACT, between facilities with a TRE index value above the cutoff level and those with a value below it, encourages the use of product recovery techniques or process modifications to reduce emissions. The values of offgas flowrate, hourly emissions, and net heating value used to calculate the TRE value for a given facility are measured at the outlet of the final product recovery device. Use of additional product recovery is expected to decrease VOC emissions and increase the total resource effectiveness associated with thermal incineration of a vent stream.

The TRE index cutoff level associated with RACT has the value 1.0. The TRE index of a process vent stream is calculated according to the following equation:

$$TRE = \frac{1}{H.E.} [a + b(FLOW)^{0.88} + c(FLOW) + d(FLOW)(H_T) + e(FLOW^{0.88})(HT^{0.88}) + f\ (FLOW)^{0.5}]$$

where:

TRE = Total resource effectiveness index value.

FLOW = Vent stream flowrate (scm/min), at a standard temperature of 20°C.*,**

H_T = Vent stream net heating value (MJ/scm), where the net enthalpy of per mole of offgas is based on combustion at 25°C and 760 mm Hg, but the standard temperature for determining the volume corresponding to one mole is 20°C, as in the definition of FLOW.*

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*See Appendix H for reference methods and procedures.

**For a Category E stream, Flow should be replaced by "Flow x $H_T/3.6$" when associated with the f coefficient.

H.E. = Hourly emissions reported in kg/hr measured at full operating flowrate.*

a, b, c, d, e, and f are coefficients. The set of coefficients which apply to a process vent stream can be obtained from Table D-1.

Table D-1 is divided into the six design categories for control equipment. These design categories differ in the amount of heat recovery achieved, in the type of heat recovery equipment used, and in the use of flue gas scrubbing for offgas containing chlorinated compounds. The amount and type of heat recovery used depends upon the offgas heating value. These design categories are defined and discussed in detail in Chapter 5. Under each design category listed in Table D-1, there are several intervals of offgas flowrate. Each flowrate interval is associated with a different set of coefficients. The first flowrate interval in each design category applies to vent streams with a flowrate smaller than that corresponding to the smallest control equipment system easily available without special custom design. The remaining flowrate intervals in each design category apply to vent streams which would be expected to [illegible] one, two, three, four, or five sets of control equipment, respectively. These flowrate intervals are distinguished from one another because [illegible] limits to prefabricated equipment sizes. The flowrate intervals and maximum offgas flowrate for each design category are presented [illegible] discussed in Chapter 5.

D.2.1 Derivation of the TRE Coefficients

The Total Resource Effectiveness (TRE) of an offgas stream is defined as the cost effectiveness of incinerating the VOC stream under consideration divided by the reference cost effectiveness ($1,600/Mg). The cost effectiveness of treating an offgas stream is determined by developing equations for the various annual cost components [illegible] the incineration system. These components include annualized capital costs, supplemental gas costs, labor costs, electricity costs, quench water costs, scrub water costs, neutralization costs, and heat recovery credit. The development of each of the cost component equations is summarized in Table D-2.

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*See Appendix H for reference methods and procedures.

TABLE D-1. COEFFICIENTS OF THE TOTAL RESOURCE-EFFECTIVENESS (TRE) INDEX EQUATION

A1. FOR CHLORINATED PROCESS VENT STREAMS, IF $0 \le$ NET HEATING VALUE (MJ/scm) ≤ 3.5:

W = Vent Stream Flowrate (scm/min)	a	b	c	d	e	f
$W < 13.5$	48.73	0	0.404	-0.1632	0	0
$13.5 < W \le 700$	42.35	0.624	0.404	-0.1632	0	0.0245
$700 < W \le 1400$	84.38	0.678	0.404	-0.1632	0	0.0346
$1400 < W \le 2100$	126.41	0.712	0.404	-0.1632	0	0.0424
$2100 < W \le 2800$	168.44	0.747	0.404	-0.1632	0	0.0490
$2800 < W \le 3500$	210.47	0.758	0.404	-0.1632	0	0.0548

A2. FOR CHLORINATED PROCESS VENT STREAMS, IF $3.5 <$ NET HEATING VALUE (MJ/scm):

W = Vent Stream Flowrate (scm/min)	a	b	c	d	e	f
$W < 13.5$	47.76	0	-0.292	0	0	0
$13.5 < W \le 700$	41.58	0.605	-0.292	0	0	0.0245
$700 < W \le 1400$	82.84	0.658	-0.292	0	0	0.0346
$1400 < W \le 2100$	123.10	0.691	-0.292	0	0	0.0424
$2100 < W \le 2800$	165.36	0.715	-0.292	0	0	0.0490
$2800 < W \le 3500$	206.62	0.734	-0.292	0	0	0.0548

B. FOR NONCHLORINATED PROCESS VENT STREAMS, IF $0 \le$ NET HEATING VALUE (MJ/scm) ≤ 0.48:

W = Vent Stream Flowrate (scm/min)	a	b	c	d	e	f
$W < 13.5$	19.05	0	0.113	-0.214	0	0
$13.5 < W \le 1350$	16.61	0.239	0.113	-0.214	0	0.0245
$1350 < W \le 2700$	32.91	0.260	0.113	-0.214	0	0.0346
$2700 < W \le 4050$	49.21	0.273	0.113	-0.214	0	0.0424

C. FOR NONCHLORINATED PROCESS VENT STREAMS, IF $0.48 <$ NET HEATING VALUE (MJ/scm) ≤ 1.9:

W = Vent Stream Flowrate (scm/min)	a	b	c	d	e	f
$W < 13.5$	19.74	0	0.400	-0.202	0	0
$13.5 < W \le 1350$	18.30	0.138	0.400	-0.202	0	0.0245
$1350 < W \le 2700$	36.28	0.150	0.400	-0.202	0	0.0346
$2700 < W \le 4050$	54.26	0.158	0.400	-0.202	0	0.0424

D. FOR NONCHLORINATED PROCESS VENT STREAMS, IF $1.9 <$ NET HEATING VALUE (MJ/scm) ≤ 3.6:

W = Vent Stream Flowrate (scm/min)	a	b	c	d	e	f
$W < 13.5$	15.24	0	0.033	0	0	0
$13.5 < W \le 1190$	13.63	0.157	0.033	0	0	0.0245
$1190 < W \le 2380$	26.95	0.171	0.033	0	0	0.0346
$2380 < W \le 3570$	40.27	0.179	0.033	0	0	0.0424

E. FOR NONCHLORINATED PROCESS VENT STREAMS, IF $3.6 <$ NET HEATING VALUE (MJ/scm):

W = Dilution Flowrate (scm/min)	a	b	c	d	e	f
$W < 13.5$	15.24	0	0	0.0090	0	0
$13.5 < W \le 1190$	13.63	0	0	0.0090	0.0503	0.0245
$1190 < W \le 2380$	26.95	0	0	0.0090	0.0546	0.0346
$2380 < W \le 3570$	40.27	0	0	0.0090	0.0573	0.0424

TABLE D-2. MATHEMATICAL FORMULATION OF ANNUAL INCINERATOR COST COMPONENTS

Component	Annualized Cost (10^3\$/yr)
1a. Annualized Capital Cost, Taxes, Insurance, and Maintenance	(number of equipment units) x (escalation factor) x (capital recovery factor + taxes, insurance, and maintenance factor) x (capital cost per unit) $= [N \times 1.056 \times 1.625 \times (0.163 + 0.10) \times (C_1 + C_2(\text{Flow}/N/0.95)^{0.88})]$
1b. Pipe Rack	[(pipe rack length) x (cost per unit length) x (installation factor) x (escalation factor) x (retrofit correction factor) x (capital recovery factor + taxes, insurance and maintenance factor)] $= 250\,[\text{ft.}] \times 32.045\,[\$/\text{ft.}] \times 1.0873 \times 0.928 \times 1.625$ $0.263 \div 1000\ \$/10^3\$$ $= 13.14 \times 0.263$ $= 3.46$
1c. Additional Ductwork	[(ductwork length) x (diameter of ductwork) x (conversion factor) x (cost per unit length) x (escalation factor) x (retrofit correction factor) x (capital recovery factor + taxes, insurance and maintenance factor)] $= 150\,[\text{ft.}] \times [(\frac{\text{Flow} \times 35.314 \times 4}{2000 \times 3.42})^{0.5} \times 12$ $\times 1.37\text{-}1.76]\,[\$/\text{ft.}] \times 1.364 \times 1.625 \times 1.087 \times 0.263$ $\div 1000\ \$/10^3$
2. Supplemental Natural Gas	(gas price) x (supplemental gas required per minute, per unit) x (number of minutes per year) x (number of equipment units) $= 4.33[\$/10^9 J] \times (G_o + (0.77 \times \text{Flow}/N) \times$ $(G_1 + G_2 \times H_T))[10^6 J/\text{min}] \times$ $0.5256[10^6 \text{min/yr}] \times N$

TABLE D-2 (Continued). MATHEMATICAL FORMULATION OF ANNUAL INCINERATOR COST COMPONENTS

Component	Annualized Cost $(10^3\,\$/\text{yr})$
3. Operating Labor, Supervisory Labor, and Overhead Labor	Operating Labor = (labor wage)(labor hours per equipment unit) (number of equipment units) = $9.79/1{,}000\ [10^3\,\$/\text{man-hr}] \times \text{labor}\ [\text{man-hr/yr}] \times N$ Supervisory Labor = 0.15 x (operating labor) Overhead Labor = 0.80 (operating labor + supervisory labor + maintenance labor) where Maintenance Labor = 0.03 (total installed capital cost) = $0.03 \times N \times [1.056 \times 1.625 \times (C_1 + C_2\ (\text{flow}/N/0.95)^{0.88}] + 13.14$ $+\ 150 \times [(\frac{\text{Flow} \times 35.314 \times 4}{2000 \times 3.42})^{0.5}$ $\times\ 12 \times 1.37\text{-}1.76]\ [\$/\text{ft.}] \times 1.364 \times$ 1.625×1.087
4. Electricity Cost	(electricity price) x (pressure drop) x (average offgas flow rate) x (flue gas:offgas ratio) x (fan equation conversion factor) x (number of hours per year) ÷ (fan efficiency) = $0.0362/1000[10^3\,\$/\text{kW-hr}] \times \Delta P[\text{in } H_2O] \times$ $0.77 \times \text{Flow}[\text{scm/min}] \times f/o[-] \times$ $0.004136[\text{kW/scm-in } H_2O] \times 8760[\text{hr/yr}] \div 0.6$ = $(0.0604) \times (\$.0362) \times \Delta P \times (0.77 \times \text{Flow}) \times f/o$
5. Quench Water Cost	(water cost) x (average offgas flow rate) x (flue gas:offgas ratio) x (water required per unit flue gas flow rate) x (number of minutes per year) = $[\$0.26\ \$/10^3\text{gal}] \times 0.77 \times \text{Flow}[\text{scm/min}] \times$ $f/o[-] \times 1.68 \times 10^{-5}[10^3\text{gal/scm}] \times 0.5256$

TABLE D-2 (Continued). MATHEMATICAL FORMULATION OF ANNUAL INCINERATOR COST COMPONENTS

Component	Annualized Cost (10^3\$/yr)
	$\times 10^6[\text{min/yr}] \times 1/1000[10^3\$/\$]$ $= \$0.26 \times (0.77 \times \text{Flow}) \times f/o \times 0.00883$
6. Scrub Water Cost	(water cost) x (average offgas flow rate) x (flue gas:offgas ratio) x (chlorine content of flue gas) x (water required per unit chlorine) x (number of hours per year) $= [0.26\ \$/10^3\text{gal}] \times 0.77 \times \text{Flow}[\text{scm/min}]$ $\times 35.314\text{scf/scm} \times f/o[-] \times$ $0.0487\left[\frac{\text{lb/hr chlorine}}{\text{scf/min flue gas}}\right]$ $\times 0.0192[10^3\text{gal/lb chlorine}]$ $\times 8760\ \text{hr/yr} \times 1/1000[10^3\$/\$]$ $= (\$0.26) \times (0.77 \times \text{Flow}) \times f/o \times (0.289)$
7. Neutralization Cost	(caustic cost) x (average offgas flow rate) x (flue gas: offgas ratio) x (chlorine content of flue gas) x (caustic requirement per unit chlorine) x (number of hours per year) $= [\$0.0515\ \$/\text{lb NaOH}] \times 0.77 \times \text{Flow}[\text{scm/min}]$ $\times 35.314\ \text{scf/scm} \times f/o[-]$ $\times 0.0487\left[\frac{\text{lb/hr chlorine}}{\text{scf/min flue gas}}\right]$ $\times 1.14[\text{lb NaOH/lb chlorine}] \times 8760[\text{hr/yr}]$ $\times 1/1000[10^3\$/\$]$ $= (\$0.0515) \times (0.77 \times \text{Flow}) \times f/o \times (17.17)$

TABLE D-2 (Concluded). MATHEMATICAL FORMULATION OF ANNUAL INCINERATOR COST COMPONENTS

Component	Annualized Cost (10^3\$/yr)
8. Heat Recovery Credit	(gas price) x (average offgas flow rate) x (energy recovery per unit offgas flow rate) x (number of minutes per year) = \$4.33[\$/10^9J] x 0.77 x Flow[scmmin] x HRF[10^6J/scm] x 0.5256[10^6min/yr] = (\$4.33) x (0.77 x Flow) x (0.5256) x HRF

The parameters that are used in Table D-2 or are required in the derivation of the TRE equation are defined as follows:

E = uncontrolled VOC emission rate, [kg/hr]
N = number of incinerator units, [-]
Flow = total design offgas flow rate, [scm/min]
f/o = flue gas to offgas ratio, [-]
H_T = heating value of offgas stream [10^6J/scm]
HRF = heat recovery factor of offgas stream, [10^6J/scm]
ΔP = scrubber pressure drop, [inches H_2O]
G_0, G_1, G_2 = coefficients in the supplemental natural gas equation with units as follows:
  G_0 [10^6J/min]
  G_1 [10^6J/scm]
  G_2 [-]

Substituting the cost expressions of Table D-2 into the TRE equation definition yields the following derivation:

TRE EQUATION DERIVATION

Equation 1:

$$\text{TRE} = \begin{matrix}\text{Total Resource}\\ \text{Effectiveness}\end{matrix} = \frac{\text{cost effectiveness of stream}}{\text{reference cost effectiveness}}$$

$$= \frac{\text{annualized cost of stream } [10^3\$/\text{yr}] \div \text{emissions reduction [Mg/yr]}}{\$1{,}600/\text{Mg}}$$

Equation 2:

annualized cost of control [10^3\$/yr] = (annualized capital cost, taxes, maintenance) + (annualized pipe rack and additional ductwork cost) + (annual supplemental gas cost) +

$$\begin{pmatrix}\text{annual operating}\\ \text{labor, supervisory}\\ \text{labor, overhead labor}\end{pmatrix} + \begin{pmatrix}\text{annual}\\ \text{electricity}\\ \text{cost}\end{pmatrix}$$

$$+ \begin{pmatrix}\text{annual quench}\\ \text{water cost}\end{pmatrix} + \begin{pmatrix}\text{annual scrub}\\ \text{water cost}\end{pmatrix}$$

$$+ \begin{pmatrix}\text{annual neutralization}\\ \text{cost}\end{pmatrix} - \begin{pmatrix}\text{annual heat}\\ \text{recovery credit}\end{pmatrix}$$

$$= [N \times 1.056 \times 1.625 \times (0.163 + 0.10)]$$

$$\times [(C_1 + C_2 (\frac{\text{Flow}}{N \times 0.95})^{0.88})]$$

$$+ 13.14 \times 0.263$$

$$+ 150 \times [\frac{(\text{Flow} \times 35.314 \times 4)^{0.5}}{2000 \times 3.42} \times 12 \times 1.37 - 1.76] \times 1.364$$

$$\times 1.087 \times 0.263 \div 1000$$

$$+ \$4.33 \times (G_o + 0.77 \times \text{Flow} \times (G_1 + G_2 \times H_T))$$

$$\times 0.5256$$

$$+ \$9.79/1000 \times 1.15 \times (\text{labor factor}) \times 1.80 + .024 \times$$

$$(1.056 \times 1.625 \times (C_1 + C_2 (\text{Flow}/N/0.95)^{0.88}) + .024 \times 13.14$$

$$+ .024 \times 150 \times [\frac{(\text{Flow} \times 35.314 \times 4)^{0.5}}{2000 \times 3.42} \times 12 \times 1.37 - 1.76]$$

$$\times 1.364 \times 1.087 \div 1000$$

$$+ \$0.0362 \times (0.0604) \times \Delta P \times (0.77 \times \text{Flow})$$

$$+ \$0.26 \times (0.77 \times \text{Flow}) \times f/o \times (0.00883) \quad \text{Category A only}$$

$$+ \$0.26 \times (0.77 \times \text{Flow}) \times f/o \times (0.289) \quad \text{Category A only}$$

$$+ \$0.515 \times (0.77 \times \text{Flow}) \times f/o \times (17.17) \quad \text{Category A only}$$

$$- \$4.33 \times (0.77 \times \text{Flow}) \times 0.5256 \times \text{HRF} \quad \text{Category A only}$$

Equation 3:

$$\underset{[\text{Mg/yr}]}{\text{emission reduction}} = \left(\begin{matrix}\text{hourly uncontrolled} \\ \text{emissions}\end{matrix}\right) \times \left(\begin{matrix}\text{number of days} \\ \text{per year}\end{matrix}\right)$$

$$\times \left(\begin{matrix}\text{number of hours} \\ \text{per day}\end{matrix}\right) \times \left(\begin{matrix}\text{capacity} \\ \text{utilization}\end{matrix}\right)$$

$$\times (\text{VOC destruction efficiency})$$

$$= E\ [\text{kg/hr}] \times 10^{-3} [\text{Mg/kg}] \times 365\ [\text{days/year}]$$

$$\times 24\ [\text{hours/day}] \times 0.77 \times 0.98$$

Equation 4:

$$\text{TRE} = \frac{\text{(annualized cost of stream) } [10^3 \$/\text{yr}]}{(1{,}600)\ [\$/\text{Mg}] \times E\ [\text{kg/hr}] \times 6.610\ [\frac{\text{Mg-hr}}{\text{kg-yr}}]}$$

$$= 0.0946 \times \frac{\text{(annualized cost of stream)}[10^3 \$/\text{yr}]}{E\ [\text{kg/hr}]}$$

$$= (0.0946/E) \times \{N \times 1.056 \times 1.625 \times (0.163 + 0.10) \times [(C_1 +$$

$$C_2(\text{Flow}/N/0.95)^{0.88}] +$$

$$13.14 \times 0.263 + 150 \times [(\frac{\text{Flow} \times 35.314 \times 4}{2000 \times 3.42})^{0.5} \times 12 \times 1.37\text{-}1.76]$$

$$\times 1.364 \times 1.087 \times 0.263 \div 1000$$

$$+ N \times 4.33 \times (G_o + 0.77 \times \text{Flow}/N \times (G_1 + G_2 \times H_T))$$

$$\times 0.5256) + N \times 9.79/1000 \times (\text{labor factor}) \times 1.80 + .024 \times 1.056 \times 1.625$$

$$\times [(C_1 + C_2\ (\text{Flow}/N/0.95)^{0.88}] + .024 \times 13.14 + .024 \times 150 \times$$

$$[(\frac{\text{Flow} \times 35.314 \times 4}{2000 \times 3.42})^{0.5} \times 12 \times 1.37\text{-}1.76] \times 1.364 \times 1.087 \div 1000$$

$$+ 0.0362 \times (0.0604) \times \Delta P \times (0.77 \times \text{flow} \times f/o)$$

$$+ [0.26 \times (0.77 \times \text{Flow}) \times f/o \times (0.00883)$$

$$+ 0.26 \times (0.77 \times \text{Flow}) \times f/o\ (0.289) + 0.0515 \times f/o$$

$$\times (0.77 \times \text{Flow}) \times (17.17)$$

$$- 4.33 \times (0.77 \times \text{Flow}) \times 0.5256 \times \text{HRF}]\}$$

Note: The terms contained in brackets [ ] apply to category A only.

Next, the TRE equation is rearranged in the form:

Equation 5:

$$\text{TRE} = \frac{1}{E}\ (\ a + b(\text{flow})^{0.88} + c(\text{flow}) + d\ (\text{flow})(H_T)$$

$$+ e(\text{flow})^{0.88}\ (H_T)^{0.88} + f\ (\text{FLOW})^{0.5}$$

Coefficients a through f are derived by substituting numeric values for all quantities except flow, H_T, and E, and then collecting like algebraic terms. Design categories B, C, and D always have the same expressions for the coefficients, while design categories A and E must be considered individually for some of the coefficients. Category A has costs associated with chlorine removal that are unique among the design categories. Category E is unique because the offgas flow is diluted prior to incineration such that the variable "flow" is replaced everywhere in Equations 2, 3, and 4 by "flow x $H_T/3.65$." These special features of categories A and E lead to variations in the expressions for coefficients a through f.

The term in the TRE equation involving coefficient a is independent of flow. The expression for coefficient a is identical for all design categories, and it consists of terms involving C1, G_o, and a labor factor. If the operating flow rate is less than 13.5 scm/min, then the expression also includes a term involving C2 because in this case the fixed value flow = 13.5 scm/min is used in the annualized capital cost expression.

- For design categories A, B, C, D, and E:
  - when flow <13.5 scm/min

$$\begin{aligned} a = {} & 0.0946 \times 1.056 \times 1.625 \times 0.263 \times N \times C1 + 0.0946 \times 13.14 \times 0.263 \\ & - 1.76 \times 150 \times 1.364 \times 1.087 \times 0.263 \times 0.0946 \div 1000 + 0.0946 \times \\ & 4.33 \times 0.5256 \times G_o \times N + N \times 0.0946 \times 0.00979 \times 1.15 \times (\text{labor} \\ & \text{factor}) \times 1.80 + 0.0946 \times .024 \times 1.056 \times 1.625 \times C1 + 0.0946 \times \\ & N \times 1.056 \times 1.625 \times 0.263 \times C2 \times (14/0.95)^{0.88} + 0.0946 \times .024 \\ & \times 1.056 \times 1.625 \times C2\ (14/0.95)^{0.88} \end{aligned}$$

$$\begin{aligned} = {} & 0.0427 \times N \times C1 + .317 + 0.2153 \times G_o \times N + 0.00192 \times N \times (\text{labor} \\ & \text{factor}) + 0.0427 \times N \times C2 \times (14/0.95)^{0.88} + .003896 \times C2 \times \\ & (14/0.95)^{0.88} \end{aligned}$$

  - when flow >13.5 scm/min

$$\begin{aligned} a = {} & 0.0946 \times 1.056 \times 1.625 \times 0.263 \times N \times C1 + 0.0946 \times 13.14 \times 0.263 \\ & - 1.76 \times 150 \times 1.364 \times 1.087 \times 0.263 \times 0.0946 \div 1000 + 0.0946 \times \\ & 4.33 \times 0.5256 \times G_o \times N + N \times 0.0946 \times 0.00979 \times 1.15 \times (\text{labor} \\ & \text{factor}) \times 1.80 + 0.0946 \times .024 \times 1.056 \times 1.625 \times C1 \end{aligned}$$

$$\begin{aligned} = {} & 0.0427 \times N \times C1 + 0.317 + (0.2153 \times G_o \times N) + (0.00192 \times N \\ & \times (\text{labor factor})) + 0.003896 \times C1 \end{aligned}$$

The term in the TRE equation involving coefficient b depends on $(\text{flow})^{0.88}$. For design categories A, B, C, and D, the expression for coefficient b includes just one term that depends on C2, and therefore, coefficient b is non-zero only when coefficient a does not include the C2 term (i.e., coefficient b is non-zero only when flow >13.5 scm/min). Coefficient b equals zero regardless of the value of flow for category E.

- For design categories A, B, C, and D:
  - when flow <13.5 scm/min

    $b = 0$
  - when flow >13.5 scm/min

$$b = 0.0946 \times N \times 1.056 \times 1.625 \times 0.263 \times C2 \times 0.95^{-0.88} \times N^{-0.88}$$
$$+ 0.0946 \times .024 \times 1.056 \times 1.625 \times C2 \times 0.95^{-0.88} \times N^{-0.88}$$
$$= N^{0.12} \times 0.0487 \times C2$$

- For design category E:

  $b = 0$ (all flow values)

The term in the TRE equation involving coefficient c depends on (flow). For design category A, the expression for coefficient c includes terms that depend on G_1, ΔP, f/o, (f/o) x (ΔP), and HRF. For design categories B, C, and D, HRF = 0 and the corresponding term does not appear in the expression for c. Coefficient c is zero for design category E.

- For design category A:

$$c = 0.77[0.0946 \times 4.33 \times 0.5256(G_1\text{-HRF}) + 0.0946 \times .0604 \times .0362 \times \Delta P \times f/o + 0.0946(.26 \times .00883 + .26 \times .289 + .0515 \times 17.17)\ f/o]$$

$$= 0.77[0.2153(G_1\text{-HRF}) + [0.000207(\Delta P)f/o] + [0.091 \times f/o]]$$

- For design categories B, C, and D:

$$c = 0.77[0.0946 \times 4.33 \times 0.5256 \times G_1 + 0.0946 \times 0.0604 \times 0.0362 \times \Delta P \times f/o]$$

$$= 0.77[0.2153 \times G_1 + 0.000207(\Delta P)f/o]$$

- For design category E:

  $c = 0$

The term in the TRE equation involving coefficient d depends on the (flow) x (H_T) product. For design categories A, B, C, and D, the expression for coefficient d consists of just one term that depends on G_2. For design category E, the expression for coefficient d consists of terms depending on G_2 and the (ΔP) x (f/o) product.

- For design categories A, B, C, and D:

$$d = 0.77 \times 0.0946 \times 4.33 \times 0.5256 \times G_2$$

$$= 0.77 \times 0.2153 \times G_2$$

- For design category E:

$$d = 0.77/3.6 \times 0.0946[4.33 \times 0.5256 \times G_1 + 0.0362 \times 0.0604 \times \Delta P \times f/o]$$

$$= 0.77/3.65[0.2153 \times G_1 + (0.000207 \times \Delta P \times f/o)]$$

The term in the TRE equation involving coefficient e depends on the $(\text{flow})^{0.88} \times (H_T)^{0.88}$ product. This product arises only in the TRE expression for category E.

- For design categories A, B, C, and D:

  e = 0 (all values of flow)

- For design category E:

  - when flow <13.5 scm/min

    $e = 0$

  - when flow >13.5 scm/min

$$e = 0.0946 \times N \times 1.056 \times 1.625 \times 0.263 \times C2 \times 3.65^{-0.88} \times 0.95^{-0.88} \times N^{-0.88} + .0946 \times .024 \times 1.056 \times 1.625 \times C2 \times 3.65^{-0.88} \times 0.95^{-0.88} \times N^{-0.88}$$

$$= N^{0.12} \times 0.0391 \times C2 \times 0.320 \times 1.0462 + 0.003896 \times 0.320 \times 1.0462 \times N^{0.12}$$

The term in the TRE equation involving coefficient $\underline{f}$ depends on (Flow).$^{0.5}$ Coefficient $\underline{f}$ is zero for design categories A, B, C, D, and E when flow <13.5 scm/min. The value of coefficient $\underline{f}$ is non-zero for all design categories only if flow >13.5 scm/min.

- For design categories A, B, C, and D:

  $f = 0$ when flow <13.5 scm/min.

- For design categories A, B, C, D, and E:

  o when flow >14 scm/min

$$f = .0946 \times 150 \times 0.263 \times 2000^{-0.5} \times 3.142^{-0.5} \times 4^{0.5} \times 1.37 \times 1.348 \times 12 \times 1.625 \times 1.087 \times 35.314^{0.5} \times 0.95^{-0.5} \div 1000 + .024 \times 0.0946 \times 150 \times 2000^{-0.5} \times 3.142^{-0.5} \times 4^{0.5} \times 1.37 \times 1.348 \times 12 \times 1.625 \times 1.087 \times 35.314^{0.5} \times 0.95^{-0.5} \div 1000$$

D.2.2 Example Calculation of the TRE Index Value for a Facility

This section presents an example of use of the TRE index equation for determination of the RACT category applicable to an individual air oxidation facility. It has been determined that the air oxidation process vent stream has the following characteristics:

1. FLOW = 284 scm/min (10,000 scfm).
2. H_T = 0.37 MJ/scm (10 Btu/scf).
3. Hourly Emissions (E) = 76.1 kg/hr.
4. No chlorinated compounds in the offgas.

Because there are no chlorinated compounds in the offgas, design Category A is not the applicable one. Categories B, C, D, and E all correspond to nonchlorinated vent streams. Because the offgas net heating value is 0.37 scm/min, Category B is the applicable one. The offgas flowrate is 284 scm/min, and therefore the second flowrate interval under Category B is the applicable one. The coefficients for Category B, flow interval #2 are:

1. $a = 16.61$
2. $b = 0.239$
3. $c = 0.113$
4. $d = -0.214$
5. $e = 0$
6. $f = 0$

The TRE equation is:

$$TRE = \frac{1}{H.E.} [a + b(FLOW)^{0.88} + c(FLOW) + d(FLOW)(H_T) + e(FLOW^{0.88})(H_T{}^{0.88}) + f\ (FLOW)^{0.5}]$$

$$TRE = (.01314)(16.61 + 0.239\ (284)^{0.88} + (0.113)(284) - 0.214\ (284)(.37) + 0 + 0)$$

$$TRE = 0.218 + 0.453 + 0.422 - 0.95 + 0 + 0$$

$$TRE = 0.798$$

Since the calculated total resource effectiveness (TRE) index value of 0.742 is less than the cutoff value of 1.0, the applicable RACT for this facility would be 98 percent VOC reduction or reduction to 20 ppm. If process modifications or increased product recovery were introduced, the product recovery vent offgas percent VOC and heating value might be sufficiently decreased that the resulting TRE value would exceed the 1.0 cutoff.

D.2.3 Calculation of Cost Effectiveness for a Facility

Because the TRE index is a cost effectiveness ratio, it is possible to calculate cost effectiveness for any vent stream given its TRE index value. The TRE index value of the facility is multiplied by the indexing constant $1,600/Mg. For the stream used in the example above, the cost effectiveness is found as follows:

TRE = 0.798

Indexing constant = \$1,600/Mg

Cost effectiveness = (0.798)(1,600) = \$1,277/Mg

D.3 RACT IMPLEMENTATION

For RACT implementation, two types of measurements are required. First, measurements must be made to evaluate the TRE index value for a given plant. Offgas flowrate, hourly emissions, and stream net heating value must be determined. Second, if a source must meet a 98 percent reduction or 20 ppmv emission requirement, then measurements of VOC reduction efficiency must be made. Appendix H identifies the recommended reference methods and procedures for implementing RACT.

APPENDIX E: COST ANALYSIS SPECIAL TOPICS

APPENDIX E: COST ANALYSIS SPECIAL TOPICS

E.1 INTRODUCTION[1,2]

The purchase cost estimates for individual pieces of control equipment are discussed in this appendix in relation to the raw vendor data on which the estimates are based. Independent vendor estimates are also compared with the purchase costs. The method of estimating installed costs from component installation factors is discussed. Graphs of the installed costs for several types of control equipment, as a function of flowrate, are presented. Graphs are also presented for total installed capital costs for the control systems, and the derivations of capital cost equations from these graphs are discussed.

E.2 CONTROL EQUIPMENT PURCHASE COSTS

E.2.1 Thermal Oxidizer

Energy and Environmental Analysis, Inc., (EEA) obtained data from the three vendors which provided combustion chamber cost data to Enviroscience. The three sets of vendor quotations agreed with each other well. The Enviroscience purchase cost curve represents a conservative "envelope" that is higher than the vendor data for all equipment sizes.

Vendor A quoted costs for four equipment sizes for each of six different incineration temperatures. Vendor B quoted costs for 14 equipment sizes for each of four different temperatures. Vendor C quoted costs for six equipment sizes for each of two different temperatures. These data constitute an abundance of observations for derivation of reasonably accurate equations for the relation of capital cost to offgas flowrate.

EEA independently obtained data from two additional vendors. Each of these quoted costs for two equipment sizes at one temperature. Their quotations essentially agreed with those of the vendors contacted by Enviroscience.

E.2.2 Recuperative Heat Exchanger

EEA obtained data from the two vendors which provided heat exchanger costs to Enviroscience. The two sets of vendor quotations agreed with each other well. The Enviroscience purchase cost curve represents an average that is roughly equivalent to the vendor curves.

Vendor A quoted costs for four offgas flowrates for each of two levels of heat recovery. Vendor C quoted costs for three offgas flowrates for each of two levels of heat recovery. Because heat exchanger costs were quoted as functions of heat exchange surface area, these data actually represent eight and six different equipment sizes, respectively. These data constitute an adequate number of observations for derivation of reasonably accurate equations for the relation of capital cost to offgas flowrate.

EEA independently obtained data from two additional vendors. One quoted costs for two offgas flowrates. The other quoted costs for two offgas flowrates for each of two temperatures. Their quotations essentially agreed with those of the vendors contacted by Enviroscience.

E.2.3 Waste Heat Boiler

EEA obtained data from one vendor which provided waste heat boiler costs to Enviroscience. The Enviroscience purchase cost curve represents this data well.

The vendor quoted costs for 10 offgas flowrates for each of three different temperatures. These data actually represent 30 different equipment sizes, and therefore constitute an abundance of observations for derivation of reasonably accurate equations for the relation of capital cost to offgas flowrate.

E.2.4 Fans

One vendor quoted costs for 13 sizes of fans. These data constitute an abundant number of observations for derivation of reasonably accurate capital cost equations.

E.2.5 Stack

One vendor quoted costs for four sizes of stacks. While these data constitute a minimal number of observations for accurate interpolation between given stack sizes, the relatively low cost of stacks compared to the rest of the control system makes extra accuracy unnecessary.

E.2.6 Ducts

Enviroscience used EPA 450/5-80-002 (The "GARD" Manual) as its source for duct costs. The source for the additional duct and the pipe support costs was a manual published by Richardson Engineering Services, Incorporated.[3]

E.3 INSTALLATION FACTORS

The Enviroscience method of estimating installed costs of combustion chamber, recuperative heat exchanger, and waste heat boiler from the original vendor cost quotations is discussed below and summarized in Table E-1. The component purchase costs represent interpolations of vendor quotations and are graphed as continuous functions of offgas flowrate. A factor of 20 percent for "unspecified equipment" was added to the budget prices of the combustion chamber and waste heat boiler. This factor was omitted for the heat exchanger. Factors were then added for 10 aspects of installation, such as insulation and piping. These factors were expressed as percentages of the budget price of the equipment in question. The overall sum of these factors plus the factor of one for the original equipment and, in two cases, the factor of 0.2 for unspecified equipment was multiplied by a factor of 1.35, which represented the impact of contingencies, fees, site development, and vendor assistance. Because the original costs seemed low, several cases were vigorously recosted. It was decided by Enviroscience that the overall installation factor would be multiplied by 1.33 to achieve a better estimate. However, Enviroscience assumed that this factor of 1.33 was due entirely to underestimates of the factors for the 10 aspects of installation. An alternative correction factor was therefore calculated which, when multiplied by the sum of the 10 installation component factors, would result in the values of the same overall installation factor as given by the 1.33 estimate. The values of this correction factor were 1.7 for the combustion chamber, 2.1 for the heat exchanger, and 1.9 for the boiler. The values of

TABLE E-1. INSTALLATION COMPONENT FACTORS (% OF BUDGET PRICE OF MAIN EQUIPMENT)

Installation Component	Combustion Chamber			Recuperative Heat Exchange			Waste Heat Boiler		
	New Source	Retrofit Labor	Retrofit Special Expenses	New Source	Retrofit Labor	Retrofit Special Expenses	New Source	Retrofit Labor	Retrofit Special Expenses
Foundation	6	9	9	6	9	9	8	12	12
Insulation	6	9	9	2	3	3	2	3	3
Structures	2	3	10	1	2	10	-	-	-
Erection	15	22	45	10	15	30	20	30	60
Piping	20	30	60	-	-	-	10	15	30
Painting	5	8	8	2	3	6	-	-	-
Instruments	15	22	22	-	-	-	4	6	6
Electrical	5	8	15	-	-	-	-	-	-
Fire Protection	1	2	2	-	-	-	1	2	2
Engineering, Freight and Taxes	29	29	29	21	21	21	29	29	29
TOTAL	104	142	209	42	53	79	74	97	142

Factors	Combustion Chamber	Heat Exchanger	Waste Heat Boiler
Budget Price	1	1	1
Unspecified Equipment	0.2	0	0.2
Total installation Component: New Source	1.04	0.42	0.74
Retrofit	2.09	0.79	1.42
Contingencies, Fees, Site Development	1.35	1.35	1.35
Overall Correction Factor	1.33	1.33	1.33
Total Installation Component Correction Factor	1.7	2.1	1.9
Overall Installation Factor: New Source	4.0	2.5	3.5
Retrofit	6.5	3.5	5.3

Formulas: (1) Overall New Source Installation Factor = (Budget Price Factor + Unspecified Equipment Factor + Total New Source Installation Component Factor) x Contingencies Factor x Overall Correction Factor
Example (Combustion Chamber): 4.0 = (1 + 0.2 + 1.04) x 1.35 x 1.33

(2) Total Installation Component Correction Factor = ((Overall New Source Installation Factor ÷ Contingencies Factor) - Budget Price Factor - Unspecified Equipment Factor) ÷ Total New Source Installation Component Factor
Example (Combustion Chamber): 1.7 = ((4.0 ÷ 1.35) - 1 - 0.2) ÷ 1.04

(3) Overall Retrofit Installation Factor = (Budget Price Factor + Unspecified Equipment Factor + (Total Retrofit Installation Component Factor x Total Installation Component Correction Factor)) x Contingencies Factor
Example (Combustion Chamber): 6.5 = (1 + 0.2 + (2.09 x 1.7)) x 1.35

the final overall new source installation factor were 4.0, 2.5, and 3.5 for the combustion chamber, heat exchanger, and waste heat boiler, respectively.

Retrofit installation factors were then developed from the new source factors. Because cramped plant conditions will make a longer time of installation necessary, the installation labor cost will increase. For each of the nine aspects of installation other than engineering, freight, and taxes, it is assumed that 50 percent of the component installation factor represents labor costs. These labor costs were assumed to double in each case. Therefore, each of the nine component factors was assumed to increase by 50 percent due to labor. Added expense was expected for four of the factors: structures, piping, erection, and electrical. Such expense might be due to a steel or concrete deck for the equipment, extra circuit breakers, and about 500 feet of extra ducting, piping, and electrical, after inclusion of the labor increase, were doubled. The factor for structures for the combustion chamber and heat exchanger was assumed to increase to 10 percent. The overall retrofit installation factors, calculated as above, for the combustion chamber, heat exchanger, and boiler were 6.5, 3.5, and 5.3, respectively.

In order that the Enviroscience total installed cost curves could be used directly, one overall retrofit-to-new source correction factor was developed. The individual correction factors for the combustion chamber, heat exchanger, and boiler were 1.625, 1.4, and 1.514, respectively. In order to give a conservative estimate of total installed costs, the value of 1.625 was used for the retrofit-to-new source correction factor.

E.4 INDIVIDUAL COMPONENT INSTALLED COSTS

Installed capital costs for a thermal oxidizer designed for a 870°C (1600°F) combustion temperature and 0.75 second residence time are given in Figure E-1. Recuperative heat exchanger installed capital costs are given in Figure E-2. Installed capital costs for inlet ducts, fans, and stack, for systems with and without heat recovery, are given in Figures E-3 and E-4, respectively. The above equipment units constitute the components of a control system for nonchlorinated vent streams.

Figures E-5 and E-6 give the installed capital costs for a thermal oxidizer at 1200°C (2200°F) and 0.75 second residence time and for a waste heat boiler, respectively. The installed capital costs of a scrubber including quench chamber are given in Figure E-7. Figure E-8 gives installed capital costs for ducts, fans, and stack for a system employing a waste heat boiler.

E.5 TOTAL CONTROL SYSTEM INSTALLED CAPITAL COSTS

Total installed capital costs of a thermal oxidation system for control of nonchlorinated vent streams are given in Figure E-9. The design conditions are 870°C (1600°F) and a 0.75 second residence time. Figure E-10 gives the total installed capital costs of a thermal oxidation system for control of chlorinated vent streams at 1200°C (2200°F). These conditions were corrected to 1090°C (2000°F) and a one second residence time. The combustion chamber volume correction factor of 1.14 represents the product of a temperature correction, combustion air flowrate correction, and residence time correction.[4]

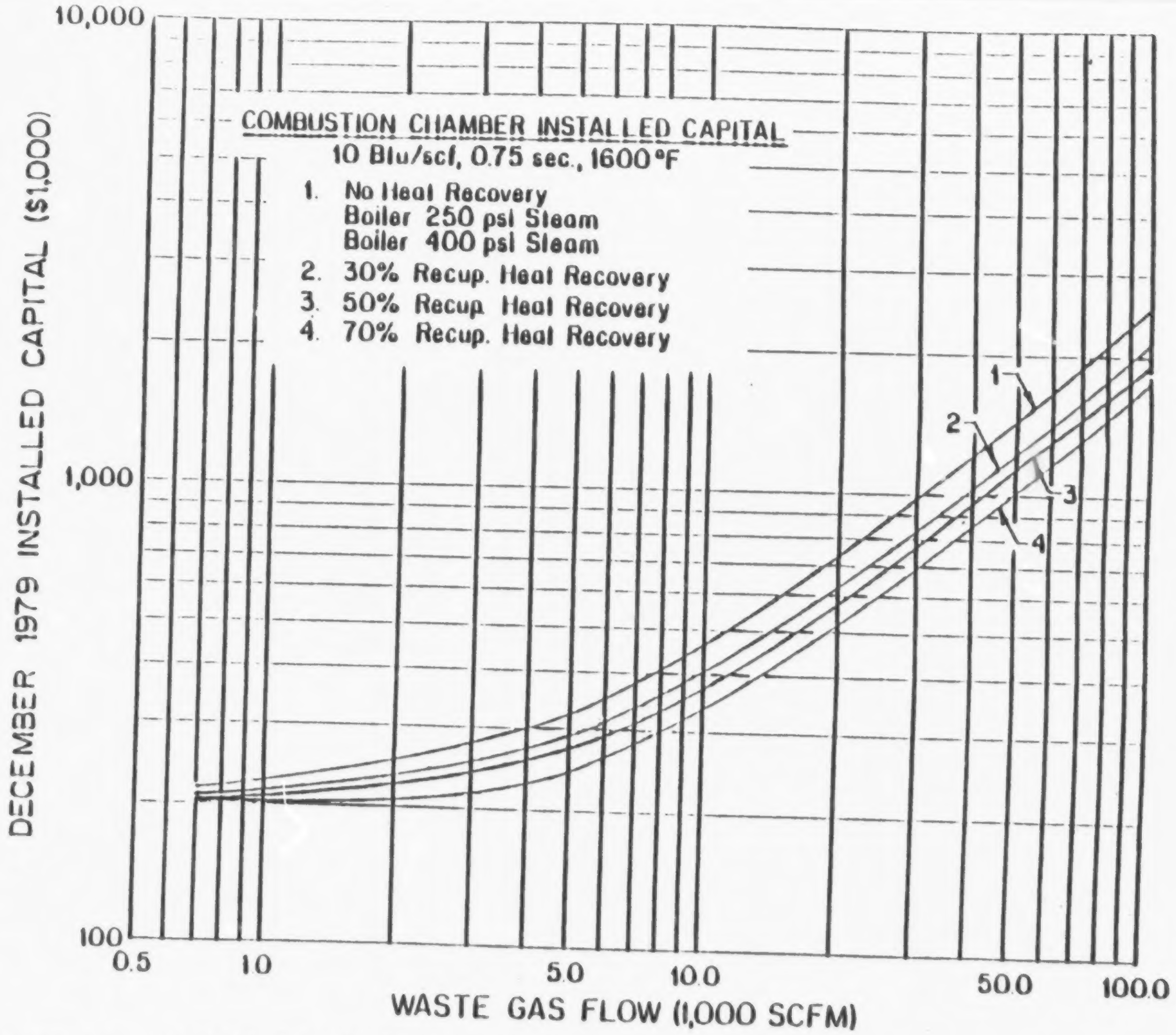

Figure E-1. Installed capital cost for the combustion chamber with waste gas heat content = 10 Btu/scf, residence time = 0.75 sec, and combustion temperature = 1600°F.

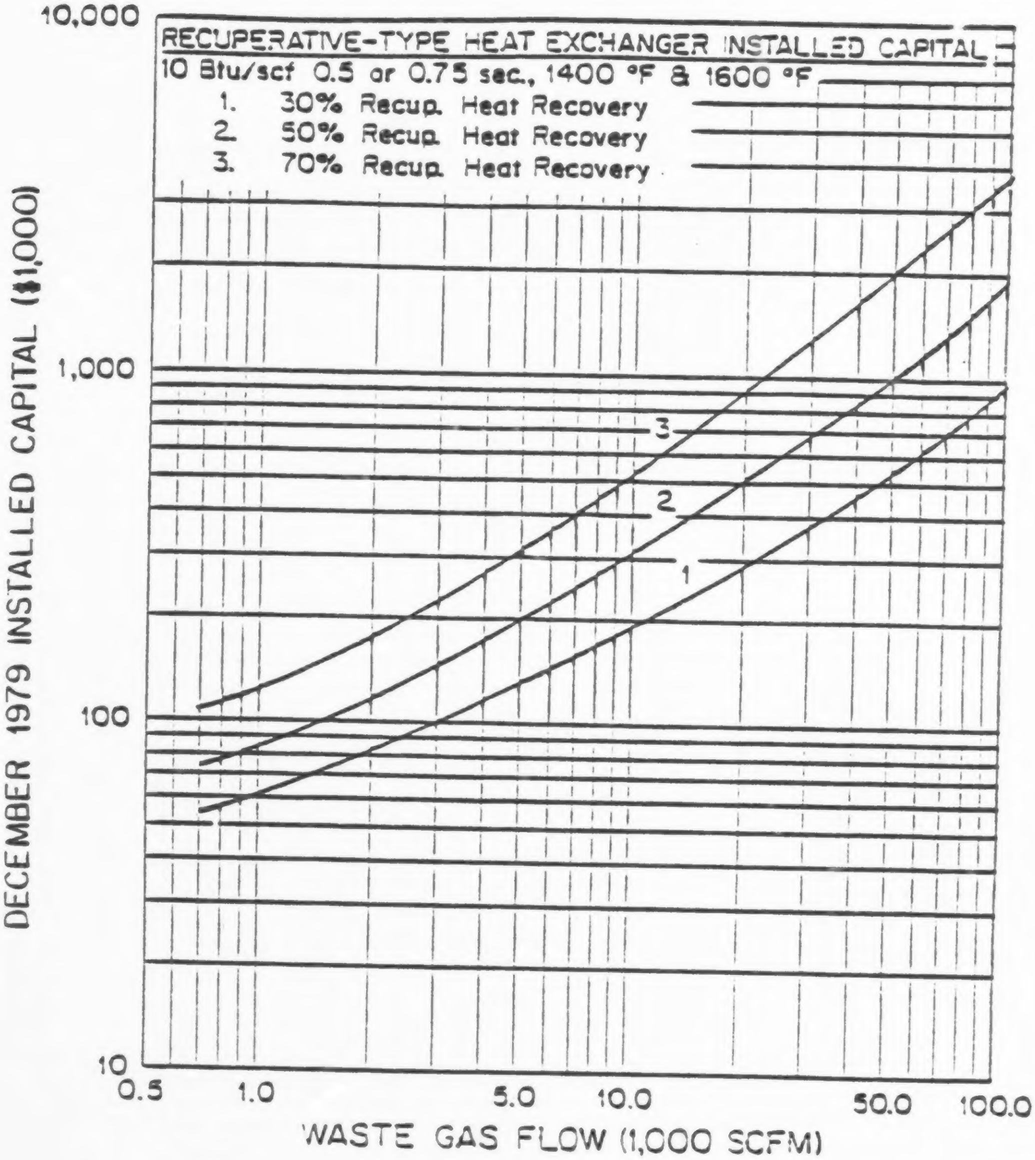

Figure E-2. Installed capital cost for recuperative-type heat exchangers with the waste gas heat content = 10 Btu/scf.

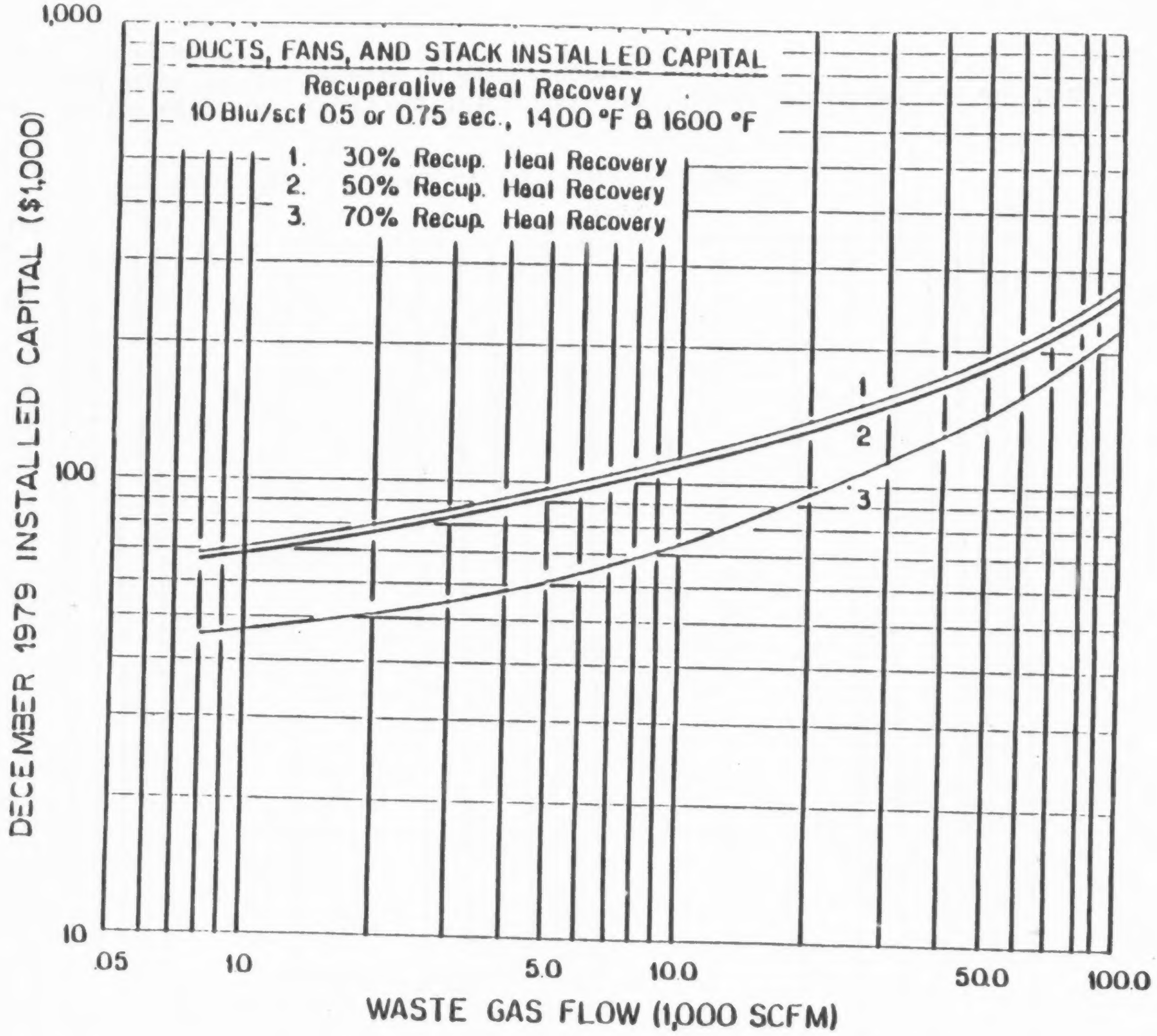

Figure E-3. Installed capital costs for inlet ducts, waste gas, and combustion air fans and stack with recuperative heat recovery.

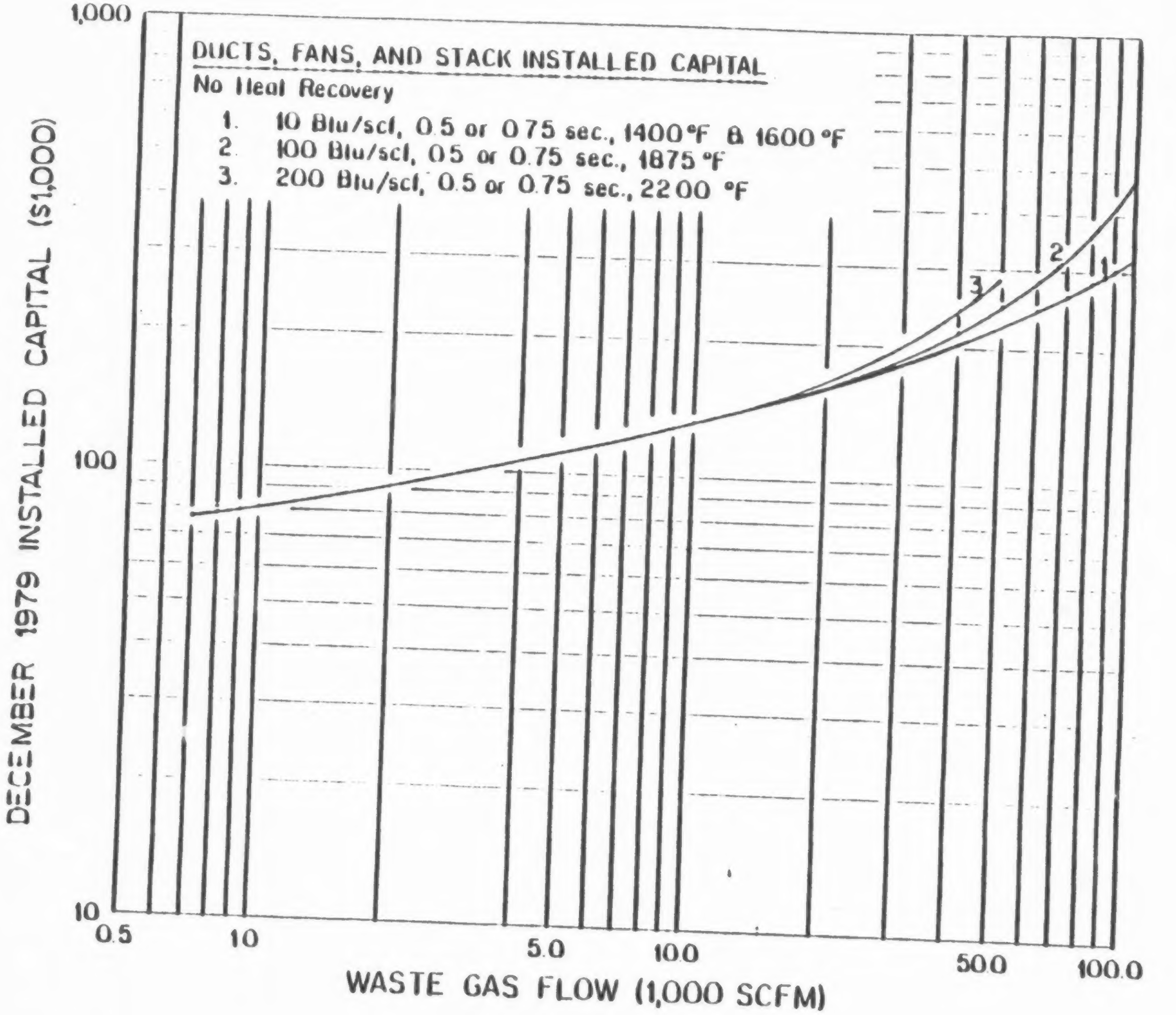

Figure E-4. Installed capital costs for inlet ducts, waste gas, and combustion air fans and stack for system with no heat recovery.

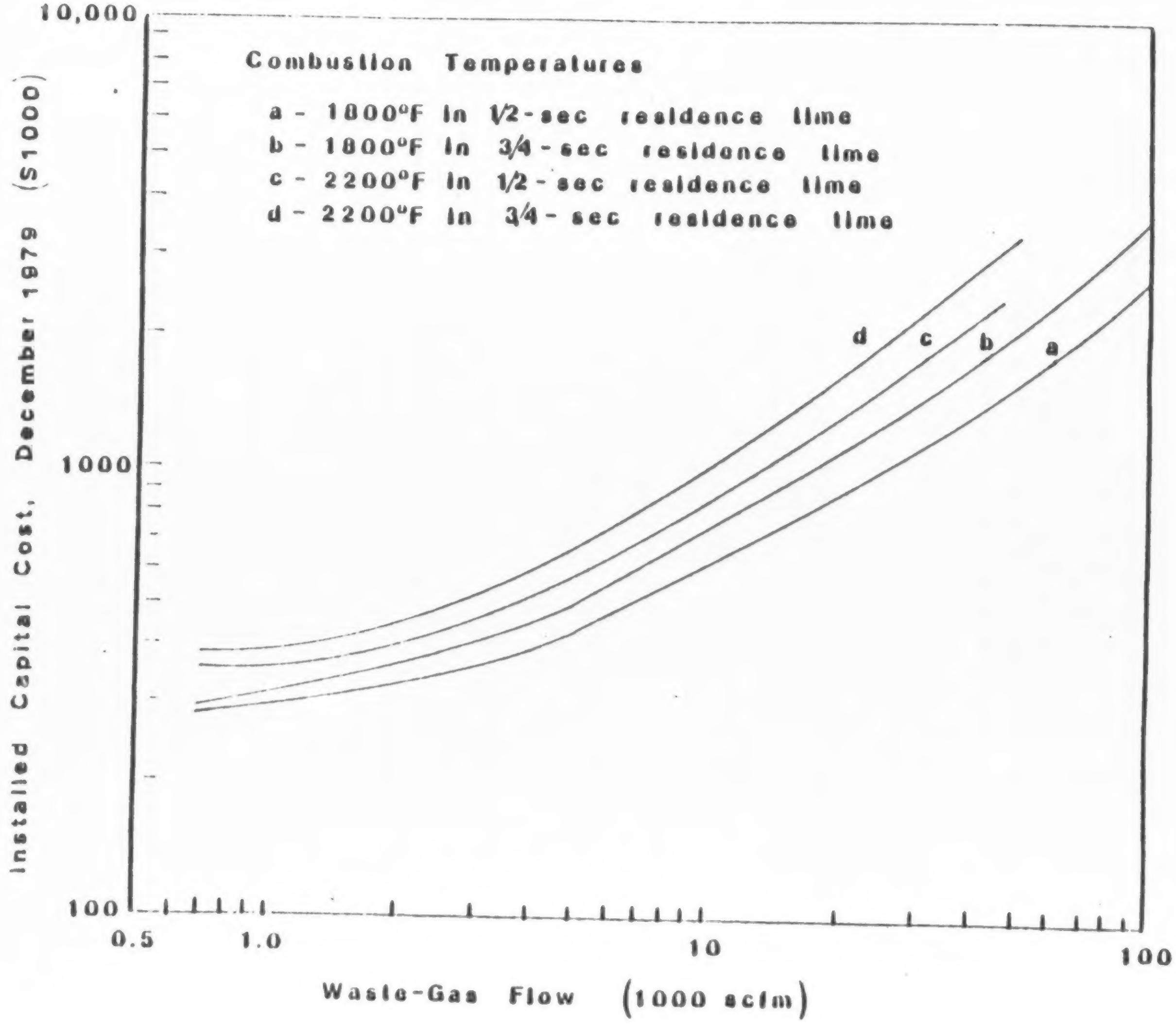

Figure E-5. Installed capital cost of thermal oxidizer at 1800 and 2200°F including incinerator, two blowers, ducts, and stack.

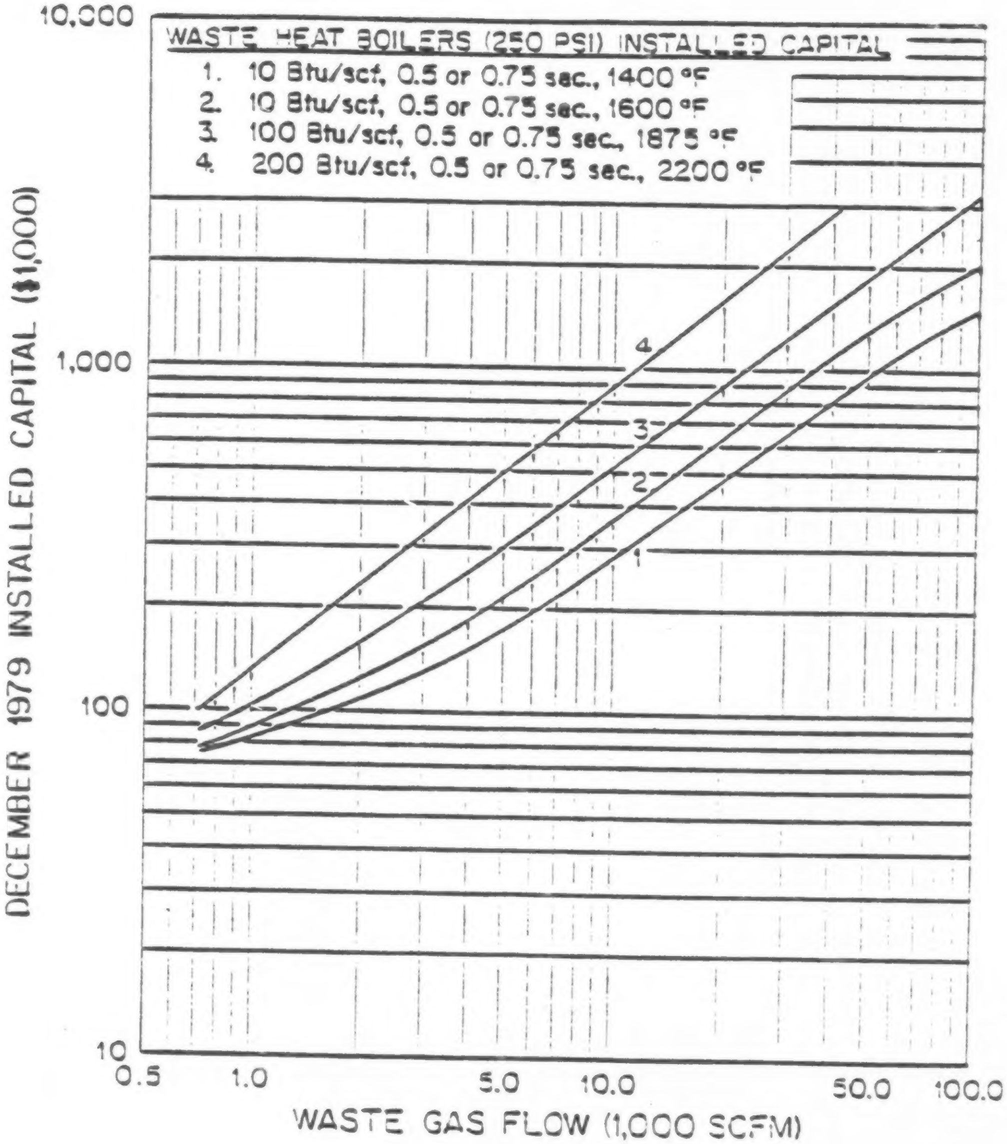

Figure E-6. Installed capital cost for waste heat boilers (250 psi).

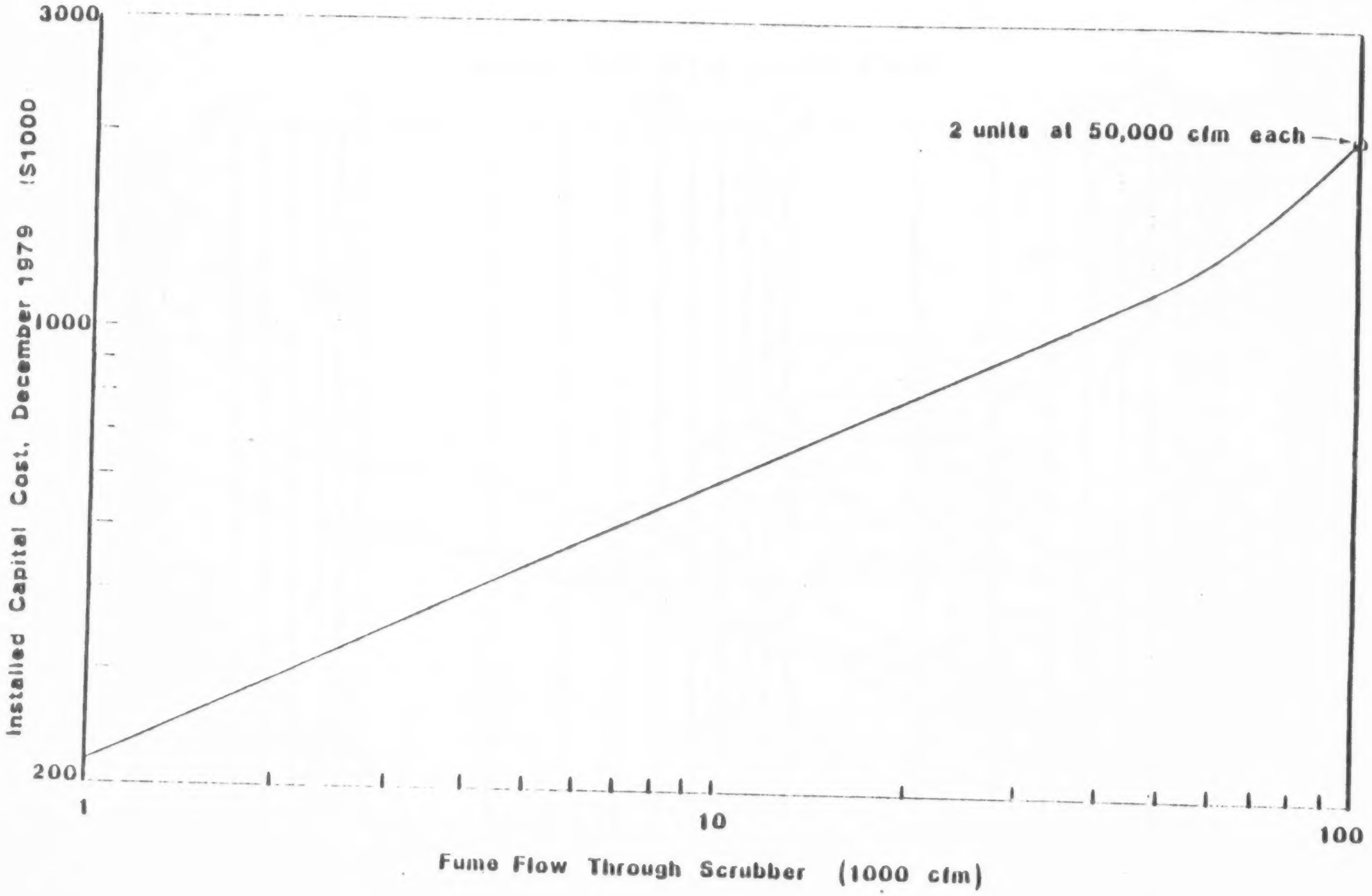

Figure E-7. Installed capital cost of the scrubber including quench chamber.

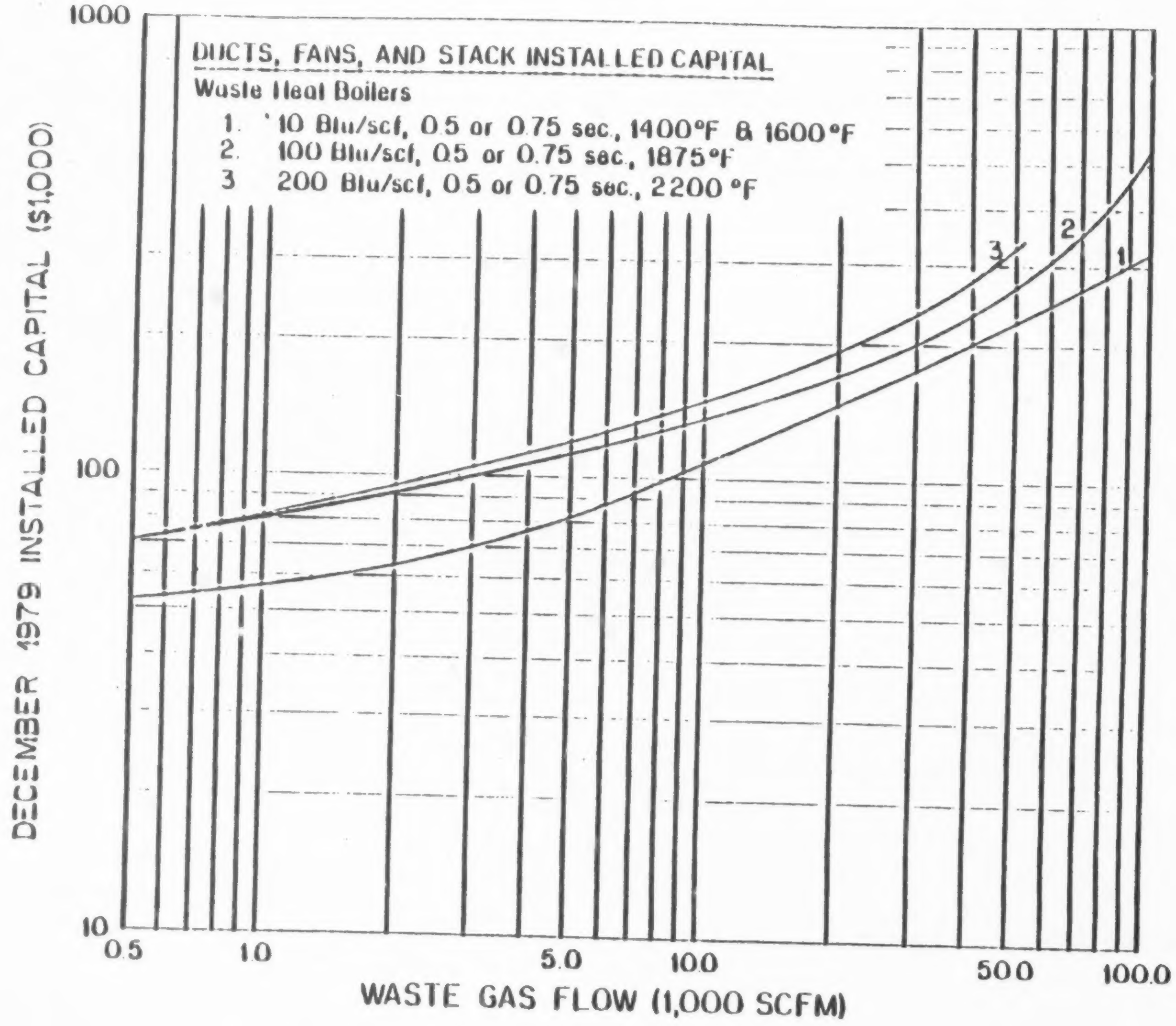

Figure E-8. Installed capital for inlet ducts, waste gas, and combustion air fans and stack with waste heat boilers.

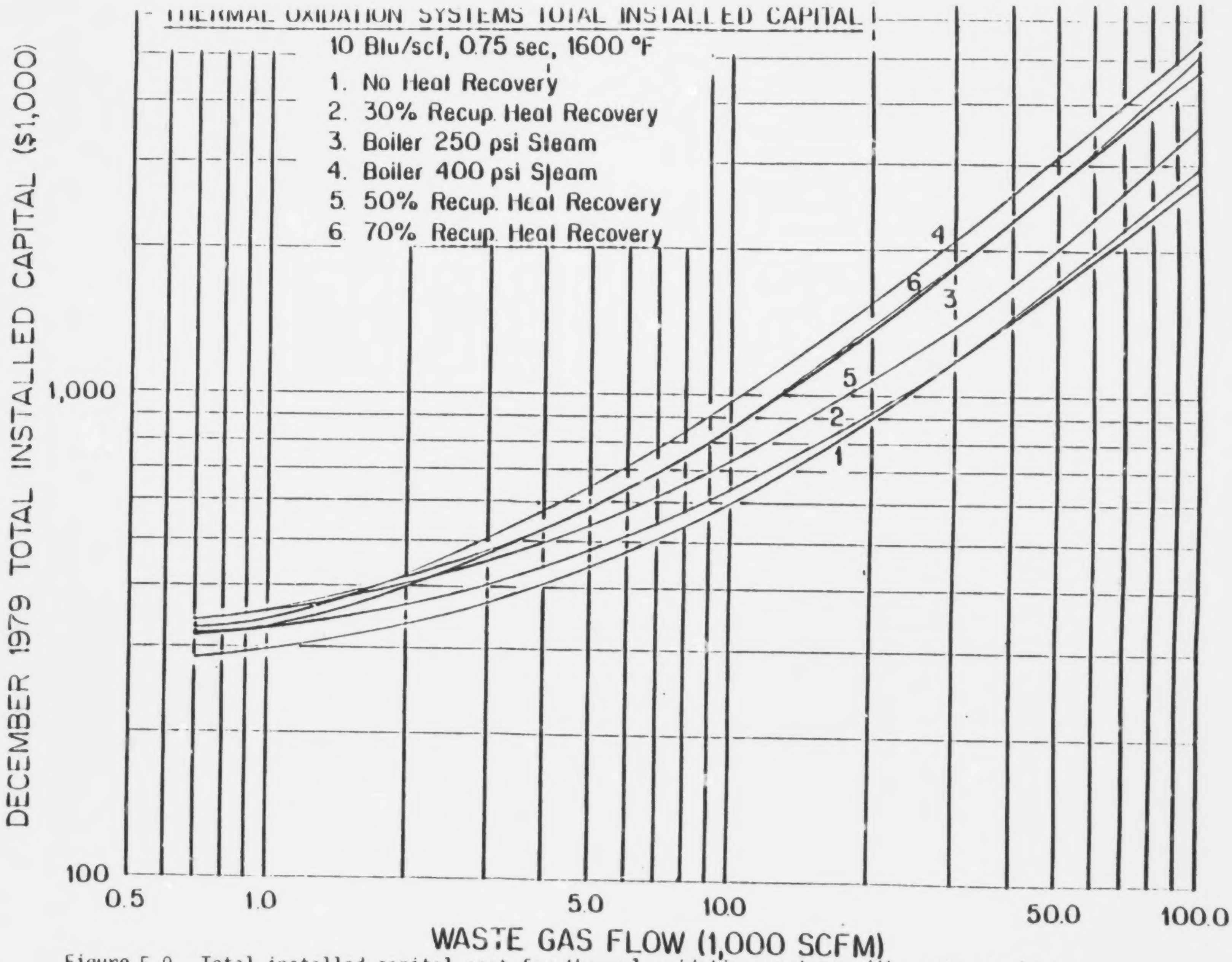

Figure E-9. Total installed capital cost for thermal oxidation systems with waste gas heat content = 10 Btu/scf, residence time = 0.75 sec, and combustion temperature = 1600^0F.

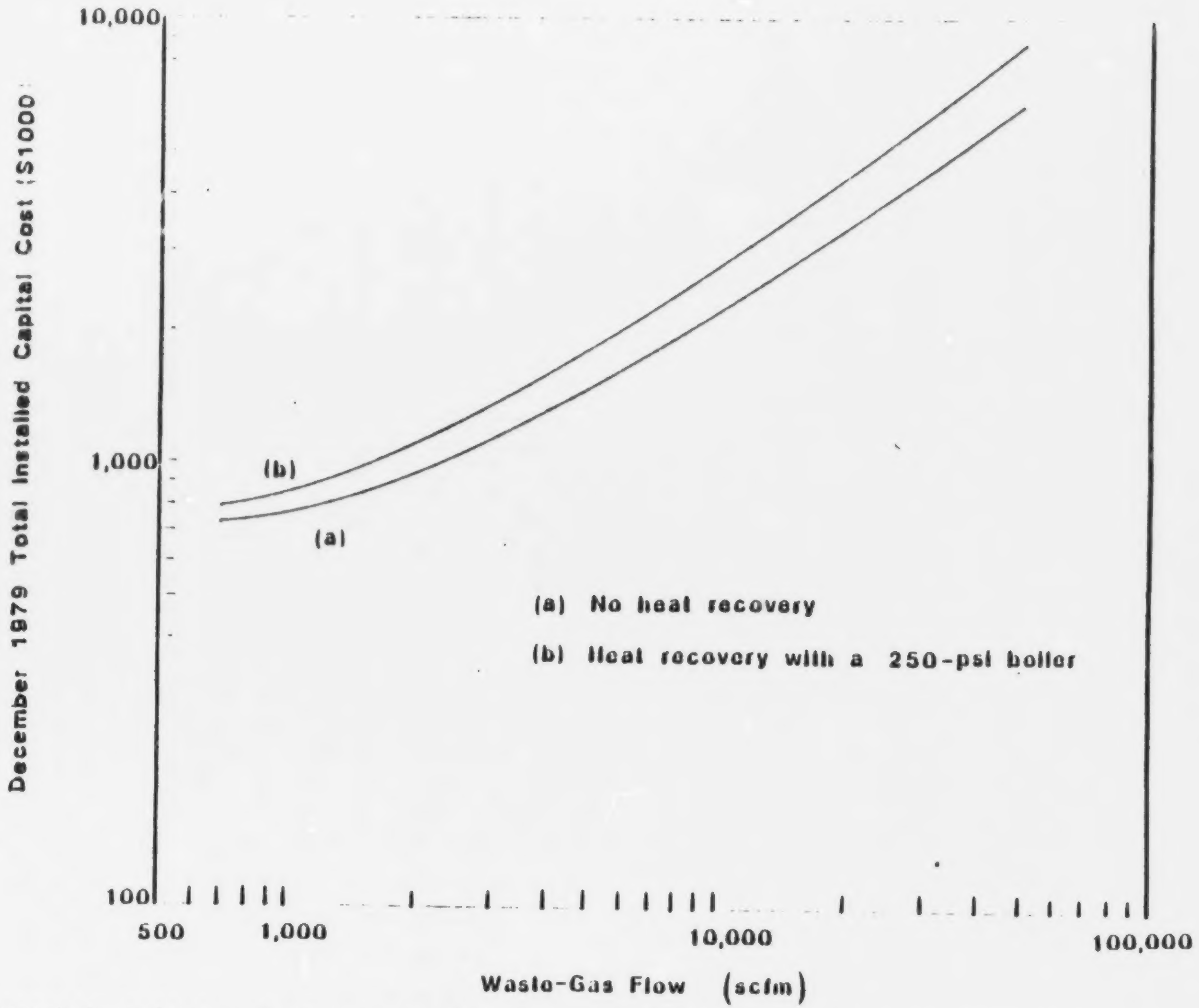

Figure E-10. Total installed capital cost for thermal oxidation systems with a scrubber at a residence time of 0.5 sec, a combustion temperature at 2200°F, and a waste gas heat content of 1 Btu/scf.

E.6 REFERENCES FOR APPENDIX E

1. Basdekis, H.S. Emissions Control Options for the Synthetic Organic Chemicals Manufacturing Industry. Control Device Evaluation. Thermal Oxidation Supplement (VOC Containing Halogens or Sulfur). EPA Contract No. 68-02-2577, November 1980. p. III-11.

2. Blackburn, J.W. Emissions Control Options for the Synthetic Organic Chemicals Manufacturing Industry. Air Oxidation Generic Standard Support. EPA Contract No. 68-02-2577. May 1979. p. III-3.

3. Richardson Engineering Services, Incorporated. Process Plant Construction Estimating Standards. 1982. San Marcos, California.

4. Memo from Galloway, J., EEA, to SOCMI Air Oxidation File. April 17, 1981.

APPENDIX F: MAJOR COMMENTS RECEIVED ON THE DRAFT CTG

APPENDIX F
MAJOR COMMENTS RECEIVED ON THE DRAFT CTG

Six letters were received as a result of an EPA request for comments on the draft CTG. Table F-1 gives a list of the commenters and their affiliations. Specific comments from these letters were grouped into the following subject areas:

(1) Applicability of the CTG;
(2) Recommendation of RACT;
(3) Cost estimation and cost effectiveness; and
(4) General.

The following sections summarize all comments received by their subject areas. The EPA response to each comment follows each comment summary. Copies of each of the comment letters are given in Appendix G.

1. APPLICABILITY OF THE CTG

1.1 Comment: Two commenters (#1, #4) raised questions concerning which chemical manufacturing processes are addressed by this CTG. Both commenters stated that the ambiguity of the list of chemicals in the CTG made it uncertain which chemicals are covered. It was their concern that because the list is given as "not exclusive," it does not properly define which of these chemicals are covered or may eventually be covered by the CTG. One commenter (#1) stated that EPA should present an all-inclusive list of chemicals in the CTG to help producers know if their processes are covered.

Response: The CTG is a guideline document for use by State agencies in establishing RACT. The final determination of RACT is left to the discretion of the State agency. However, it must be noted that the RACT recommendation and background information presented in the CTG pertain to synthetic organic chemicals produced via air oxidation processes.

The thirty-six (36) chemicals listed in Table 2-1 represent the air oxidation chemicals which the Agency has identified. It is possible that chemicals not included in the list could be produced by newly developed air oxidation processes in the future or complete information on all chemicals produced by air oxidation was not available to the Agency. Thus, it is recommended that any air oxidation chemicals not identified by the Agency be covered by the recommended RACT. The supporting information and equations for RACT are applicable to all air oxidation processes used in manufacturing synthetic organic chemicals.

1.2 Comment: One commenter (#2) stated that oxyhydrochlorination/ethylene dichloride plants should not be included in the scope of this CTG. The commenter based this view on the unique vent stream control problems present in the chlorinated solvent industry, as well as the location of the existing EDC plants. All but two affected EDC plants are located in Texas and Louisiana, where vent incineration is already required. One of the remaining two is located in California and is already subject to strict regulation. The last plant is located in Kentucky and the commenter felt that it could be adequately addressed through the Kentucky State Implementation Plan.

TABLE F-1. LIST OF COMMENTERS AND AFFILIATIONS

Comment no.	Commenter and affiliation
1	Dr. Robert A. Romano, Manager Air Programs Chemical Manufacturers Association 2501 M Street, Northwest Washington, D.C. 20037
2	Mr. M. M. Skaggs, Jr., P.E. Senior Environmental Engineer Diamond Shamrock Chemicals Company 1149 Ellsworth Drive Pasadena, Texas 77501
3	Mr. D. E. Park, Director Corporate Environmental Affairs Ethyl Corporation Post Office Box 341 Baton Rouge, Louisiana 70821
4	Mr. J. D. Reed, General Manager Environmental Affairs and Safety Standard Oil Company (Indiana) 200 East Randolph Drive Chicago, Illinois 60601
5	Mr. A. H. Nickolaus, Chairman CTG Subcommittee Texas Chemical Council 1000 Brazos, Suite 200 Austin, Texas 78701-2476
6	Mr. D. C. Macauley, Manager Environmental Affairs Union Carbide Corporation Ethylene Oxide/Glycol Division Post Office Box 8361 South Charleston, West Virginia 25303

Response: The Agency acknowledges that unique vent stream control problems exist for ethylene dichloride plants because of the presence of halogenated compounds in their process vent streams. However, the Agency has accounted for this in the cost analysis for RACT. The analysis incorporates in the TRE equation the cost associated with scrubbing incinerator flue gases containing halogenated compounds. This scrubbing cost includes the cost of a scrubber and auxiliaries, a quench chamber, makeup water, and caustic. Thus, the TRE index for a halogenated vent stream will accurately represent the cost of scrubbing incinerator flue gases.

The cost associated with disposal of sodium chloride from the neutralized scrubbing water of halogenated vent streams is based on direct discharge which results in a negligible expense. Thus, the Agency considers the cost associated with the disposal of sodium chloride to be negligible. All but one existing air oxidation facility with halogenated vent streams are located near the coast where the brine can be discharged either directly or indirectly to salt water at relatively low costs. The remaining facility will either sell the HCl solution, or, if no market exists, will neutralize the wastewater with caustic and dispose of the brine solution in a nearby freshwater river. Thus, brine disposal costs are expected to be insignificant for all facilities.

Finally, it is important to note that the Agency considers it proper to include EDC plants in the scope of this CTG even if only one (1) plant were to be affected. As stated in Chapter 1, EPA has permitted States to defer the adoption of RACT regulations on a category of sources of volatile organic compounds (VOC) until after the EPA published a control techniques guideline (CTG) for that VOC source category. Although presently the only EDC plant which may potentially be affected by the CTG is located within an attainment area in Kentucky, there is a possibility that the area could experience a change in status to nonattainment. Thus, the CTG may be used to develop RACT that would affect this EDC plant. Also, the list of chemicals in Table 2-1 is intended to identify all known air oxidation chemicals without regard to control status. Plants already subject to control would not be affected by the RACT recommendation in this CTG and would incur no costs.

1.3 Comment: Two commenters (#1, #4) stated that the draft CTG does not clearly indicate which process vents are to be controlled. One commenter (#1) said that the CTG should be revised to specify that it is not intended to cover vents resulting from a reactor bottoms stream in cases where the stream (which consists of liquids or solids with entrained air) is ultimately passed through product purification operations. Another commenter (#4) said that even though discussions with EPA pointed out that vents from product purification are not covered under the CTG, the CTG itself does not make this clear.

Response: Process vents that result from the product purification of a reactor bottoms stream will not be covered by this CTG. For example, liquid phase air oxidation reactors have two process streams, one liquid and one gaseous. The liquid stream usually contains the desired product and is taken to product purification. The gaseous stream containing nitrogen, unreacted oxygen, CO_2, and some VOC is sent to product recovery to collect reactants or additional product before being vented to the atmosphere. The TRE calculations should be applied to this offgas stream after the final product recovery device.

1.4 Comment: Two commenters (#1, #4) raised questions concerning the calculation of the total resource effectiveness (TRE) index on processes with multiple vent streams or where the stream is split after leaving the process. For example, one case was given where a portion of the vent stream (i.e., side stream) is taken for use as a transport gas and another case was where the stream is vented separately to the atmosphere from each of two scrubbers in series. Both commenters requested these cases be clarified as to whether the TRE should be applied to the separate streams or to the combined stream.

Response: If a side stream has a process use (such as a transport gas or a gas blanket) the TRE should be calculated for it separately. This calculation is done separately because there is a possibility that the side stream will pick up additional VOC contamination when used in process operations. For example, a side stream used as a gas blanket in a storage facility containing an organic liquid may collect additional VOC from the evaporation of stored organics.

If the side stream has no process use the TRE should be calculated on the combined stream. The measurement of parameters for the TRE equation is made at the outlet of the final product recovery device where VOC is reclaimed for beneficial reuse. For the VOC recovery to be considered beneficial reuse, the material must be recycled, sold, or used in another part of the process. For example, consider a case where two scrubbers in series are both used to recover VOC for beneficial reuse and part of the total stream is vented to the atmosphere separately from each scrubber. The measurement of flow rate, heat content, and VOC emissions should be made at both vents. These measured parameters should then be combined for use in the TRE equation. The measured flow rates and VOC emission rates would be added to yield the aggregate flow and emission rate. The aggregate heating value can be obtained by calculating a weighted average for the separate vent streams.

In cases where VOC from one of the two scrubbers in series is wasted, the measurement of parameters for the TRE equation for that part of the stream is made at the inlet to the scrubber from which the VOC is wasted. These are added to the other measured parameters as previously described. In cases where the VOC from both scrubbers in series is wasted, the measurement of parameters for the TRE equation is made prior to the inlet of the first scrubber. If this were not required, the owner or operator of an affected facility could choose to use a scrubber to reduce VOC emissions, comply with the standards by attaining a TRE index value above the 1.0 cutoff, but cause a negative environmental impact through the disposal of the recovered VOC to land or water. If the TRE value were to be calculated after a scrubber from which all VOC was wasted, then EPA would be neglecting the need to limit the pollution of land and water. To provide a means of compliance with the standards by the collection and disposal of VOC emissions would impede the improvement of environmental quality.

2. RECOMMENDATION OF RACT

2.1 Comment: Two commenters (#4, #5) said that the CTG does not fulfill its purpose of providing State and local air pollution control agencies with the information they need to make their own assessment of RACT. The commenter also said that RACT requirements are dictated in Chapter 4 of the CTG without explanation of the basis for RACT or the alternatives considered. Several commenters (#1, #2, #5, #6) voiced concern over the lack of alternatives available for RACT. They said that the draft CTG does not adequately address alternative control technologies which may be as effective as thermal incineration. Other control methods identified by the commenters for consideration as RACT are flares and catalytic incinerators.

Response: The Agency believes that there is ample flexibility within the RACT recommendation described in the CTG document. The RACT recommendation outlined in Chapter 4 of the CTG does not mandate that a specific control technique be used for an air oxidation facility. Rather, the RACT recommendation sets percent reduction requirements and/or emission limits which have been demonstrated to be achievable by available technology. The RACT recommendation permits the use of alternative control techniques such as flares and catalytic incinerators, as long as the emission reduction requirements and/or limits are achieved. Available data show that these devices are capable of achieving the emission reduction requirements outlined in the RACT recommendation.

In order to analyze the impacts of RACT, a technology or technologies had to be identified that would be available to all potentially affected SOCMI air oxidation facilities and would achieve the largest feasible emission reductions at a reasonable cost. Thermal oxidation was the only technique that met both of these qualifications for the industry as a whole, and thus it was selected for the impact analysis. The RACT recommendation would allow the use of any alternative to thermal oxidation if the owner or operator of an air oxidation facility were to determine that another technique would be more appropriate. However, if an alternate technique is used the 98 percent reduction or 20 ppmv emission limit specified in the RACT recommendation must be met.

The RACT recommendation has additional flexibility in that the emission reduction requirements or emission limits do not have to be met if a facility can maintain a TRE index greater than 1.0. The operator of a facility having a TRE index less than 1.0 may upgrade product recovery or modify the process to reduce emissions and raise the TRE index above 1.0. This would enable the facility to avoid the specific emission reduction requirements specified in the RACT recommendation. The benefits from compliance with RACT in this manner are: (1) lower control costs; (2) recovered products, by-products, and feedstocks; and (3) lower energy consumption.

The Agency also believes that there is sufficient information within the CTG to enable State and local air pollution agencies to make their own assessments of RACT. As stated in Chapter 1 of the CTG, the purpose of the document is to review existing information and data concerning the cost of various control techniques to reduce emissions. Since the document is general in nature, it may not fully account for variations within the source category. However, this CTG provides a substantial information base for the State and local agencies to proceed with their own assessments of RACT.

2.2 Comment: A observation was made by a commenter (#6) that even though the CTG includes a statement that RACT is not specifically to be met through the use of thermal oxidation (page 4-1), it is the commenter's belief that the criteria of 98 percent emission reduction or a VOC concentration of 20 ppmv can only be met by thermal oxidation. Thus, the criteria do not allow industry a choice of alternative control technologies.

Response: The Agency has determined that 98 percent emission reduction can be met by several control techniques on streams for which these techniques apply. Available data show that efficiencies of 98 percent and above can be achieved by catalytic oxidation (Martin, N., Catalytic Incineration of Low Concentration Organic Vapors. U. S. Environmental Protection Agency, Research Triangle Park, North Carolina. 1981. EPA-600/2-81-017). In addition, tests have also shown that flares can achieve at least 98 percent destruction efficiency, (McDaniel, M., Flare Efficiency Study. U. S. Environmental Protection Agency, Research Triangle Park, North Carolina. September 1982. EPA-600/2-83-052). Finally, the Agency believes that most steam generating units (e.g. boilers and process heaters) can achieve a VOC destruction efficiency of at least 98 percent or reduction to 20 ppmv provided that the vent stream is introduced into the flame zone. These units are generally operated at temperatures higher than and residence times longer than those conditions necessary to achieve 98 percent destruction efficiency. Also, it is to the economic advantage of the owners of facilities using steam generating units to operate these units with stable flowrates and adequate mixing so that maximum combustion efficiency is achieved. Therefore, there are many devices that can achieve a 98 percent destruction efficiency on streams for which they apply. The applicability of these devices depends upon stream characteristics and can only be determined on a case-by-case basis.

2.3 Comment: One commenter (#1) stated that while thermal oxidation is the only method analyzed in the CTG as a candidate for RACT, it is not true that the control efficiency of thermal oxidation is much less dependent on process and waste stream characteristics than other control techniques, nor is thermal oxidation economically applicable to all air oxidation processes. The commenter said that destruction efficiency of thermal oxidizers is dependent on flame stability, which in turn depends on the composition, heating value, and flowrate of the waste gas. In addition, some process conditions will not lend themselves to efficient operation of thermal oxidation and, therefore, other control techniques may be applicable and their use should be encouraged.

Response: Available data show that the control efficiency of thermal oxidation is much less dependent upon process and waste characteristics than are other control techniques such as catalytic oxidizers and various product recovery devices. The applicability and effectiveness of product recovery devices such as condensers, absorbers, and adsorbers may be greatly affected by the vent stream flowrate, water content, temperature, VOC concentration, and VOC properties such as solubility, molecular weight, and liquid/vapor equilibrium. In general, where catalytic oxidizers are applicable, information shows that 98 weight percent destruction can be achieved. However, some air oxidation vent streams may have characteristics which would limit the applicability of catalytic oxidizers. For example, vent streams with high heating value or vent streams with compounds that may deactivate the catalyst may not be suitable for applying catalytic oxidizers. Catalysts can be deactivated by compounds sometimes present in the waste stream, such as sulfur, bismuth, phosphorus, arsenic, antimony, mercury, lead, zinc, or tin. Deactivation of the catalyst may also occur at high temperatures.

Thermal oxidation, on the other hand, is much less dependent on process and vent stream characteristics as described above, and it is the only VOC control technique that can achieve 98 percent emission reduction or 20 ppmv outlet concentrations for all SOCMI air oxidation processes. However, the RACT recommendation does not discourage the use of other control techniques. The RACT recommendation would allow the use of any alternative to thermal oxidation provided that the 98 percent reduction or 20 ppmv emission limit specified in the RACT recommendation is met. Also, the use of product recovery devices is allowed insofar as the owner or operator of an affected facility may upgrade recovery equipment to raise the TRE value above 1.0 and thus, avoid having to reduce VOC emissions by 98 percent or to 20 ppmv.

Although thermal oxidizer efficiency is dependent on flame stability, it is relatively easy to maintain flame stability so that 98 percent destruction efficiency is ensured. The required efficiency can be attained when mixing of the VOC stream, combustion air, and hot combustion products from the burner is rapid and thorough. This enables the VOC to reach the desired combustion temperature in the presence of enough oxygen for a sufficient period of time for the oxidation reaction to reach completion. Chamber design and burner/baffle configurations provide the turbulent flow necessary for good mixing.

The commenter's concern that thermal oxidation may not be economically applicable to all air oxidation processes is addressed by the inclusion of a TRE cutoff in the RACT recommendation.

2.4 Comment: Two commenters (#2, #6) suggested that the criteria adopted as RACT be relaxed. It was the belief of one commenter (#2) that a 95 percent control efficiency should be adopted. As a result of the 95 percent control efficiency, the commenter felt that greater nationwide emission reductions would occur and gave two reasons to support this opinion. First, because the lower control efficiency would allow the use of catalytic oxidation and flares for RACT in addition to thermal incinerators, more process streams would require incineration using the $1,600/Mg cost-effectiveness criterion. Secondly, because today's higher costs for natural gas would encourage design of many new thermal incinerators to use a more polluting fuel such as oil or coal, the use of catalytic oxidation or flares would avoid additional SO_2, NO_x, and particulate emissions resulting from the fuel. This commenter said that the additional cost of achieving 98 percent control, as opposed to 95 percent, is not justified by the additional emission reductions achieved at 98 percent control. The commenter also said that in order to correctly examine cost effectiveness, one must compare the incremental cost to remove the last ton of a pollutant, as well as average cost effectiveness.

Both commenters said that catalytic oxidation has not been properly addressed as a RACT alternative. One of these commenters (#2) felt that the text of the CTG makes it appear that the 98 percent emission reduction criterion was selected specifically to exclude catalytic oxidation.

Response: Catalytic oxidation and flaring have not been excluded by the RACT recommendation. As indicated in the response to Comment 2.1, the RACT recommendation does not mandate that a specific control technique be used for an air oxidation facility. The RACT recommendation permits the use of alternative control techniques, as long as the emission reduction requirements and/or limits are achieved. Thermal incineration is not specifically required by the RACT recommendation. It is merely the control technique upon which the RACT recommendation and the impacts of RACT are based. The Agency expects that in some cases other control techniques, such as catalytic oxidation and flaring, will be used. As stated in the response to Comment 2.2, where catalytic oxidizers and flares are applicable, information shows that these techniques can achieve 98 percent destruction efficiency.

In determining the level of control which represents RACT, the Agency examined emission data from incinerators already operating within the industry as well as incinerator tests conducted by the Agency and by chemical companies. The data show that all the new, well-operated incinerators were achieving 98 percent destruction efficiency. Also, at the lower temperature and shorter residence time associated with lower efficiencies, some VOC may not come into contact with sufficient oxygen at a high enough temperature to enable the oxidation of VOC to proceed to completion. As a result, there is greater chance that partially oxidized organic compounds (e.g., aldehydes) and carbon monoxide may be generated. Thus, the Administrator determined that 98 percent destruction efficiency represents RACT.

One commenter (#6) stated that by lowering the percent reduction requirement and, consequently, allowing other less expensive control devices to be used, more process streams would require combustion using the $1,600/Mg cost effectiveness criterion and more emission reductions would occur. This assumption is incorrect because the RACT recommendation specifies that all facilities calculate cost effectiveness using an equation based on thermal incineration, which is the only control technique universally applicable to the industry. Thus, even though a facility using a less expensive device would have a lower projected cost effectiveness than that projected using the equation based on thermal incineration, the higher value would be used to determine whether the costs of combustion are reasonable and a combustion device should be installed.

The commenter also indicated that the use of catalytic oxidation or flares would avoid additional SO_2, NO_x, and particulate emissions resulting from thermal incinerators using oil or coal. However, the Agency believes that at least in the foreseeable future, virtually all incinerators will use natural gas for supplemental fuel. Most existing incinerators currently use natural gas and are expected to continue to use it because the price and availability have not changed so dramatically that this trend will not continue.

3. COST ESTIMATION AND COST EFFECTIVENESS

3.1 Comment: Four commenters (#1, #2, #5, #6) questioned the basis for the cost estimates developed for the CTG. All four commenters stated that the CTG ignores substantial costs associated with the purchase, construction, and operation of a thermal incinerator. Two commenters (#1, #5) mentioned that the disposal cost of NaCl from scrubbers is not insignificant as stated in the CTG. One commenter (#1) mentioned that energy recovery (as steam) is not feasible in many processes, especially where halogenated compounds are present. Two of the commenters (#2, #5) stated that the costs associated with the addition of a thermal incinerator to an existing process are underestimated due to the omission of costs for siting, bringing utilities and services to the site, and piping and instrumentation connections. One commenter (#5) also noted that the 150 feet estimated by the EPA for ductwork to the thermal incinerator is too short. He felt that due to explosion hazard, many plant owners would not feel comfortable locating an ignition source so close to a process, and suggested that 300 to 500 feet would be a more representative figure.

Three commenters (#2, #5, #6) stated that the TRE index formula should be revised to consider the omissions described above and other costs such as: wastewater treatment expenses, variability in the cost of building materials (carbon steel cannot be used for construction in EDC plants), down time for heat recovery units on thermal incinerators, maintenance costs, operating supplies, and other capital and annualized costs. Estimates for additional costs given by one commenter (#5) are: operating supplies (9-33 percent of operating labor), laboratory expense (10-20 percent of operating labor), technical oversight (over 25 percent of operating labor), and general plant overhead (50-70 percent of operating labor). The commenter recommended that a factor of 40 percent of operating and maintenance labor be added to account for these administrative and implementation costs.

Another commenter (#2) gave the following additional cost factors: heat recovery unit down time, maintenance costs, operating supplies (20 percent of operating labor), and laboratory expenses (15 percent of operating labor). This commenter (#2) also stated that the TRE formula should be revised to allow a company to use its true costs and thus take regional cost differences into consideration.

One commenter (#5) stated that the estimates for annualized costs noted in the CTG are too low. This commenter gave a comparison between his organization's estimates and the CTG estimates. By their estimation (in June 1980 dollars), total annualized costs will be $803,140, as compared to the EPA estimate of $519,550. These costs are for a vent stream with a flow rate of 284 SCM/min, heat content of 0.37 MJ/SCM, VOC emissions of 76.1 Kg/hr, and no chlorinated compounds in the offgas.

Response: The procedure used in this cost analysis was developed using input from many sources, including the Chemical Manufacturers Association (CMA) and the Texas Chemical Council (TCC). The procedure is sufficiently detailed for the purpose of this cost analysis, which is to develop cost estimates that adequately represent control costs anticipated to be incurred by the majority of plants in the industry. The cost estimates developed for this standard, while not "worst case," are intended to be representative for the industry as a whole, and, therefore, should not significantly underestimate or overestimate the costs for any individual facility. The Agency believes that in some cases both minor underestimates and minor overestimates may occur due to the site-specific nature of the costs associated with installing incinerators at existing facilities. However, the cost algorithms should not result in any significant inaccuracies. Although several commenters mentioned that some items were omitted in the cost algorithms, many of these items are actually not omissions at all.

The cost associated with disposal of sodium chloride from the neutralized scrubbing water of halogenated vent streams is based on direct discharge which results in a negligible expense. This is believed to be representative of the situation that all air oxidation facilities will face. All but one existing air oxidation facility with halogenated vent streams are located near the coast where the brine can be discharged at a relatively low cost either directly or indirectly into the ocean or into a brackish stream. The remaining facility will either sell the HCl solution directly, or if no market exists, will neutralize the wastewater with caustic and dump the brine solution into a nearby freshwater river. Thus, brine disposal costs are expected to be insignificant for all existing air oxidation facilities and no change in the costing procedures will be made.

Two commenters stated that the algorithms have omitted significant costs that will be incurred when adding control devices to existing facilities. The costs identified as being omitted were for siting, bringing utilities to the site, and piping and instrumentation connections. This statement, however, is inaccurate. Siting and piping/instrumentation costs are actually included in the capital cost installation factor. Furthermore, the Agency believes that the cost associated with adding a control device at an existing facility is not underestimated. To account for difficulties associated with adding a control device to an existing process, a retrofit correction factor of 1.625 was used in estimating total installed capital costs. This increases the total installed capital costs by about 63 percent. The costs for bringing utilities to the site are not included because the control device (i.e., thermal incinerator) will most likely be located in the proximity of the process unit where utilities are readily accessible.

Two commenters recommended the inclusion of a factor of 35-40 percent of operating and maintenance labor to account for heat recovery unit down time, operating supplies, laboratory expenses, technical oversight, and general plant overhead. Some of these items have been incorporated in the maintenance labor and materials factor; the taxes, insurance, and administrative charges factor; and the operating labor rate which includes overhead. Also, even if the commenter's factor were incorporated in the cost algorithms, total annualized costs would increase only by about 2 percent.

Other factors and assumptions were included in the algorithms to avoid underestimating costs incurred by facilities using combustion to control VOC. These assumptions were made to ensure that control equipment sizes and supplemental gas requirements were not underestimated. First, vent streams were assumed to contain no oxygen to maximize estimated combustion air requirements. Most streams, while not containing 21 percent oxygen, have some smaller percentage of oxygen present. Therefore, the assumption of no oxygen ensures that no underestimate will occur for the equipment size, the combustion air flow rate, and the amount of supplemental natural gas needed. Second, actual offgas flow rate was inflated by 5 percent in calculating costs, which inflated gas consumption and equipment size by 5 percent. Third, the temperatures and residence times assumed for cost estimation purposes (1,600°F/.75 sec for nonhalogenated streams, 2,000°F/1 sec for halogenated streams) were higher than those conditions generally necessary to achieve a 98 percent VOC destruction efficiency, as discussed in Appendix A of the CTG document. These higher temperatures and residence times would result in a larger equipment size and higher gas consumption. Fourth, the overall installation factors assumed for new sources were 4.0, 2.5, and 3.5 for the combustion chamber, heat exchanger, and waste heat boiler, respectively. These factors were all higher than the EPA GARD Manual factor of 2.17 (EPA-450/5-80-002).

Upon evaluating all the public comments, several changes were made in the cost algorithms. The ductwork length used in the cost analysis was changed from 150 feet to 300 feet and 250 feet of pipebridge supports for the ductwork was added. The ductwork length increase was based on specifications provided by The Industrial Risk Insurers (IRI) and the National Fire Protection Association (NFPA). These are groups which present recommended distances for safely locating combustion sources from process units in chemical plants. An additional 100 feet was added to the IRI and NFPA recommendation to account for routing the stream around equipment and to the perimeter of the process unit before routing it away from the process unit. The 300-foot figure is believed to be more representative of industry conditions, and is within the range recommended by the one industry commenter on this item.

The gas price used in the cost algorithms was revised to reflect the upward trend of national gas prices. Since gas prices are projected to rise more rapidly than inflation, the Agency believes it is important to use a 1980 base-year gas price that will reflect these rising prices. As explained in Chapter 5, the gas price was projected for the year 1990 weighted geographically and then was deflated to 1980 dollars (the base year for all costs used in the CTG document). This was done to obtain a representative gas price on a national basis that would be incurred by facilities.

The labor price and utility prices such as electricity, water, and caustic were also revised. These prices were revised to be more representative of 1980 costs, which the TRE equation is based on. Although these prices were originally based on 1980 prices, further examination showed that more representative prices could be used. These prices have the same basis as the labor and utility prices for NSPS's using the TRE concept.

3.2 Comment: One commenter (#5) stated that the absence of design algorithms in the CTG prevented his organization from properly comparing EPA capital cost estimates with actual thermal incinerator costs. He suggested that EPA have a construction firm perform a cost estimation on the example case given in Appendix E of the CTG.

Response: The incinerator cost algorithms presented in Appendix E are derived from cost equations outlined in Chapter 5. The underlying assumptions used in developing these cost equations are explained in this chapter and the referenced documents. The cost data in this CTG were based on the two IT Enviroscience thermal oxidizer evaluation documents that specifically apply to air oxidation processes [(a) Basdekis, H. S., Emissions Control Options for the Synthetic Organic Chemicals Manufacturing Industry. Control Device Evaluation. Thermal Oxidation Supplement (VOC Containing Halogens or Sulfur). EPA-450/3-80-028d , November 1980. (b) Blackburn, J. W. Emissions Control Options for the Synthetic Organic Manufacturing Industry. Control Device Evaluation. Thermal Oxidation. EPA-450/3-80-028d, July 1980]. Enviroscience has been involved in designing these types of emission control devices for industry and was determined to be qualified to develop costs estimates for this CTG. Furthermore, these procedures have been extensively reviewed by industry and vendor representatives and revisions have been made where appropriate.

3.3 Comment: A commenter (#2) noted that the CTG used out-of-date costs and that more recent costs should be examined. The commenter mentioned that the cost factors used in the proposed TRE formula have not been examined in five years, even though they were inflated to 1980 levels. This commenter further stated that adopting a CTG on outdated costs is poor scientific and technical practice. The commenter recommended the formula be revised to allow the use of present and projectable future costs based on the date of application.

Response: The Agency has reviewed the costing procedure and believes that the current costs are not outdated. As mentioned in the response to comment 3.1, upon reviewing all the public comments, the gas, labor and other utility factors were reviewed and necessary revisions were made. These revisions were made to ensure that costs most representative of 1980 would be used and, where appropriate, projectable future costs would be incorporated in the cost algorithms. Since natural gas prices are rising more rapidly than inflation, the Agency believes it is appropriate to use a base-year gas price that will reflect these rising prices. The labor and other utility factors such as electricity, water, and caustic were also revised and are now on the same basis as the labor and other utility prices for the new source performance standards using the TRE concept. The labor and other utility prices are not expected to rise more rapidly than inflation and, thus, will not affect the validity of the TRE equation.

The equipment costs used in the algorithms were based on the most recent data available when the costing was done. Costs were updated from 1979 dollars to 1980 dollars using fabricated equipment indexes for chemical plants. The Agency believes that it is neither feasible nor necessary in terms of accuracy of the TRE equation to continually update equipment costs during the development of the CTG. This is because equipment costs are not expected to rise at a rate significantly higher than the general inflation rate. General inflation does not affect the results of the TRE equation. Regardless of whether it is expressed in 1980 or 1984 dollars, the TRE equation yields the same value. The TRE index value of a particular stream represents the ratio of the cost-effectiveness associated with incineration of that stream to the cost-effectiveness cutoff of $1,600/Mg. If the cost-effectiveness value for a particular stream is increased due to general inflation, the reference cost-effectiveness cutoff would experience the same increase since both values are based on the same cost assumptions. Thus, the ratio will remain the same, and the TRE index value will be unchanged.

3.4 Comment: One commenter (#5) stated the cost-effectiveness cutoff of $1,600/Mg is too high. The commenter based this belief on the fact that most VOC source control costs (in prior NSPS studies) have not exceeded $1,000/Mg and questioned why EPA would propose a CTG that is more stringent than a NSPS. This commenter also requested clarification of the base year dollars used in the CTG. It was not clear if the 1980 dollars were updated to current dollars in the CTG. If 1980 dollars are used, the commenter pointed out that the cutoff of $1,600/Mg becomes $1,970/Mg when inflated to 1984 dollars.

Response: The Agency believes that a cost-effectiveness cutoff of $1,600/Mg (1980 dollars) is a reasonable upper limit for the application of the RACT recommendation. The Agency evaluated several factors in analyzing the RACT alternatives. These included the energy, environmental (air and water quality, solid waste), cost, cost effectiveness and product price impacts associated with these alternatives. The RACT alternative represented by a $1,600/Mg cutoff was selected because of the potential for unreasonable economic impacts (i.e., increases in the price of chemical products) or unreasonable cost-effectiveness values at more stringent RACT levels.

Although a facility could theoretically incur a cost effectiveness as high as $1,600/Mg, it is probable that lower cost-effectiveness values will be incurred. The reasons for this are (a) other less expensive control techniques are likely to be used by facilities; and (b) the inherent flexibility within the recommended RACT encourages the use of product recovery improvements that will reduce the cost incurred by individual facilities while also reducing the national energy impact. The RACT impact analysis assumes that incinerators will be used to reduce VOC emissions by 98 weight percent. However, many facilities may opt to use boilers, process heaters, flares, or catalytic oxidizers. When these devices are used, the costs of control may be reduced from the cost of thermal incineration. Furthermore, the RACT recommendation does not require the control of VOC emissions if a TRE index greater than 1.0 is maintained. The EPA believes that many facilities having TRE indexes of 1.0 or less will upgrade product recovery to reduce VOC and raise their TRE values above 1.0. This will also significantly reduce the costs of control incurred by the industry. To study the potential impacts of requiring air oxidation facilities to control VOC emissions using thermal incinerators, the Agency developed a statistical profile of facilities which is assumed to represent all existing air oxidation facilities. An analysis of these facilities indicated that the highest cost effectiveness that a facility will actually incur as a result of installing a combustion device is about $1,000/Mg. This analysis also shows that facilities in the statistical profile with cost-effectiveness values above $1,000/Mg would be able to upgrade product recovery to achieve a TRE greater than 1.0.

3.5 Comment: Two commenters (#5, #6) questioned the inconsistencies of TRE formulae and the tables of coefficients in the CTG as opposed to the Air Oxidation Processes Draft Background Information Document (BID). One commenter (#6) felt that the wrong table of coefficients (page E-3 of the July 1981 draft CTG) was printed in the CTG. Another commenter (#5) said that the inconsistencies between the BID and the CTG were caused by the use of different annualized cost factors. Some of the differences in the cost factors are:

	BID	CTG
Operating Labor	$13.08/hr	$11.10/hr
Electricity	$ 0.02616/kWh	$ 0.0490/kWh
Natural Gas	$ 4.78/GJ	$ 2.40/GJ
Caustic Price	$ 0.0436/lb	$ 0.0563/lb

Source: BID Table 8-7, July 1981 Draft, CTG Table 5-7.

One commenter (#6) noted that a TRE index of 1.0 in the CTG corresponds to a value of $1,600/Mg, while a 1.0 index in the BID corresponds to a value of $886/Mg.

Response: There are valid reasons for the difference between the set of TRE coefficients in Table E-1 of the July 1981 draft CTG and the set of coefficients presented in the BID. The primary reasons for the difference are (1) a different reference cost-effectiveness value used in the TRE equation for the draft CTG; and (2) a retrofit correction factor was incorporated in the total installed capital cost component for the TRE equation within the draft CTG. The retrofit factor increases the capital cost by 62.5 percent to account for difficulties associated with adding a control device to an existing process.

Although not a primary cause for the difference in TRE coefficients, the different cost factors do account for some variation. However, as indicated in the responses to comments 3.1 and 3.3, the gas, labor, and other utility factors were revised. These revisions were made for two main reasons: (1) to account for the fact that natural gas prices are rising more rapidly than inflation; and (2) to use labor and other utility factors that are more representative of 1980 costs. The gas, labor, and other utility factors now have the same basis as the factors used in the air oxidation NSPS. The slight differences between factors are due to the different base year used in the CTG (i.e., 1980) compared to the NSPS (i.e., 1978).

There is a valid reason that TRE index will correspond to different cost-effectiveness values in the CTG and in the proposal BID. The calculation for determining a TRE index differs between the two documents although the method used is essentially the same. In the CTG, the TRE index of a stream represents the ratio of the cost-effectiveness of that stream to a reference cost-effectiveness of $1,600/Mg (i.e., the cost-effectiveness cutoff). In the BID the TRE index of a stream represents the ratio of the cost-effectiveness of that stream to a different reference cost-effectiveness. This reference cost effectiveness is $88,660/Mg (i.e., the most expensive plant to control in the statistical profile) divided by 100 or $886/Mg. Thus, it is correct that a TRE index of 1.0 corresponds to $1,600/Mg in the CTG and $886/Mg in the BID. Both TRE indexes are correct and reflect the differences reference cost effectiveness values used, as well as the fact that a retrofit correction factor was used in the CTG. It should be noted that the Agency intends to change the reference cost effectiveness used in the BID to $1,900/Mg (i.e., the cost-effectiveness cutoff). This change will cause the TRE index of 1.0 to correspond to $1,900/Mg.

3.6 Comment: One commenter (#6) stated that measurements for determining TRE should be based on the emissions that are actually being released to the atmosphere, regardless of whether the last step in the process is (a) product recovery, (b) energy recovery, or (c) a less than ideal existing emissions control device.

Response: The measurement for determining the TRE index of a stream must be based on emissions exiting the final recovery device where the VOC from that device is reclaimed for beneficial use (i.e., recycled or sold) rather than for waste disposal. The reasons for this are discussed in the response to Comment 1.4.

Any existing energy recovery device or emissions control device that combusts the offgas would be permitted by the CTG and no additional control would be required. Thus, for cases (b) and (c) mentioned by the commenter, where both are combustion devices, TRE measurements would not be necessary because the facilities would already be in compliance with the RACT requirement. Any existing energy recovery device or emissions control device that does not combust the offgas would be required to measure for the TRE index after the final product recovery device where VOC is reclaimed for beneficial reuse.

4. GENERAL

4.1 Comment: One commenter (#4) stated that his organization's data analysis indicates that fewer than 25 plants have the potential to be controlled more effectively under the CTG than under present controls and, therefore, he questions the need for the CTG.

Response: The Agency believes that many facilities have the potential to be controlled more effectively under RACT as outlined in the CTG than under present controls. Of the four States identified in the CTG as having state regulations applicable to SOCMI air oxidation processes, none has a requirement more stringent than the RACT recommendation. Furthermore, even if fewer than 25 plants could be controlled more effectively under RACT, the Agency would pursue development of the guidelines through publication of the CTG document. The reason for this is that one air oxidation facility can emit a substantial amount (5,000 Mg or more) of VOC annually.

4.2 Comment: Two commenters (#1, #2) questioned apparent conflicting TRE cutoff values in the draft CTG. They noted that in Appendix D (page D-1), the TRE cutoff value used for RACT is given as 2.9 but it is given as 1.0 in both Section 5 (page 5-28) and Appendix E (page E-1).

Response: In Appendix D (page D-1), the TRE cutoff of 2.9 is a typographical error, 1.0 is correct. The text has been revised to reflect this correction.

4.3 Comment: Two commenters (#1, #4) stated that the general description of the Air Oxidation Industry is vague and does not accurately detail the industry.

Response: Although the description of the Air Oxidation Industry is presented in a general way, the actual group of sources intended for coverage by this RACT is clear. The recommended RACT is applicable to those chemicals listed in Table 2-1 as well as any other synthetic organic chemicals which are produced by air oxidation. A description of an air oxidation unit process is given on page 2-1.

4.4 Comment: One commenter (#1) said that the discussion of Illinois State Regulations, in Chapter 3, was incorrect and should be clarified. The commenter stated that the Illinois regulation actually requires VOC emission controls at one of three levels: (1) 8 pounds/hr, (2) 10 ppmv equivalent methane, or (3) 85 percent destruction. It is stated in the CTG that Illinois limits all VOC emissions to 100 ppm equivalent methane.

Response: Illinois State Regulations limit emissions of organic material to eight pounds per hour unless controlled by: (a) thermal or catalytic incineration capable of meeting emission limits of 10 ppm equivalent methane, or 85 percent hydrocarbon destruction, (b) a vapor recovery system that adsorbs, absorbs, or condenses at least 85 percent of the uncontrolled organic material, or (c) any other control device approved by the Illinois Agency as being capable of reducing uncontrolled organic material emissions by 85 percent. The Illinois Regulations in the CTG have been corrected.

4.5 Comment: One commenter (#1) suggested that in Chapter 5, it should be clarified that "E" (hourly emissions) is just the VOC emissions and "Flow" is the flow of the vent stream.

Response: The text has been amended to clarify these terms.

4.6 Comment: A commenter (#2) said that NOx emissions from coal combustion are erroneously attributed to fuel nitrogen content on page A-20. These emissions are conventionally thought of as being independent of fuel nitrogen.

Response: Both the Utility Boiler and the Stationary Gas Turbine Background Information Documents (BID) note that the contribution of NO_x by fuel nitrogen can indeed be significant when burning high nitrogen fuel. Additionally, in the July, 1979 Proceedings of the Second NO_x Control Technology Seminar hosted by the Electric Power Research Institute, J. J. Marshall and A. P. Selker of Combustion Engineering, Inc., presented a paper stating that fuel NO_x can account for 30 to 75 percent of total NO_x emissions in pulverized coal firing. The text of the CTG was altered to read, "By contrast, fuel nitrogen can account for a significant percentage of total NO_x emissions in the combustion of heavy oils, coal and other high nitrogen fuels, such as coal-derived fuels and shale oils."

4.7 Comment: The following general observations were made by four commenters (#1, #2, #5, #6) on the July 1981 draft CTG.

- There is an apparent typographical error on page E-3. Line A2 should read "For Chlorinated Process Vent Streams, if 3.5 FNet Heating Value (MJ/Nm3)." (commenter #1)
- Printing errors on pages 3-17 to 3-20 have resulted in the omission of one portion of the text and duplication of other portions. One commenter (#2) requested a revised copy of the document and suggested that the comment period be reopened to allow the omitted section to be reviewed. (commenters #2, #6).
- The CTG uses "Nm3" for normal cubic meters. This is confusing since N is the standard symbol for Newtons. (commenter #5)

Response:

- The text was corrected to read ". . . if 3.5 FNet Heating Value (MJ/Nm3)."
- This section of the text has been corrected to include the omitted material. The comment period was not reopened because the omitted material contains no controversial information.
- Nm3 should not be confused with Newtons, because the unit Newton is not used in the context of the CTG.

4.8 Comment: Three commenters (#2, #3, #4) pointed out the following errors in Table 2-6.

- Diamond Shamrock sold its LaPorte, Texas EDC/VCM facility to B. F. Goodrich Corporation in 1981. (commenter #2)
- The correct corporate name of Diamond Shamrock's Deer Park Plant is Diamond Shamrock Chemicals Company. (commenter #2)
- The two Ethyl Corporation facilities manufacturing 1,2-dichloroethane by air oxidation are incorrect listings. (commenter #3)
  - The Ethyl Corporation's Baton Rouge, Louisiana 1,2- dichloroethane air oxidation process unit was shut down in January 1983.
  - The Ethyl Corporation's Pasadena, Texas 1,2-dichloroethane unit does not use air oxidation.
- Amoco Standard does not manufacture acetone and phenol in Richmond, California and does not have a plant there. (commenters #1, #4)

Response:

- The text has been changed to read B. F. Goodrich Corporation.
- The text has been changed to read Diamond Shamrock Chemicals Company.
- These two Ethyl plants were deleted from the table.
- The Amoco-Standard plant was deleted from the table.

FOREWORD

The following memorandum examines the potential of facilities with a TRE index below the cutoff to upgrade product recovery and raise their TRE index above the cutoff. It should be noted that this memorandum is based on a July 1981 draft of the CTG, which includes TRE coefficients based on a cutoff of 2.9 (equivalent to $1,600/Mg). In subsequent drafts of the CTG, the TRE index cutoff was changed to 1.0, reflecting a change in the reference cost effectiveness value used in the TRE index equation. New TRE coefficients were derived that are based upon the TRE index cutoff of 1.0. The TRE index cutoff of 1.0 is still equivalent to $1,600/Mg. Thus, the change in the TRE index cutoff has not invalidated the examination presented in the memorandum. The following product recovery analysis is based on the costing procedures set forth in the July 1981 draft at the CTG and does not reflect the costing changes discussed in this appendix. However, these costing changes would not alter the results to such an extent that the conclusions reached as a result of this analysis would be different.

RADIAN
CORPORATION

MEMORANDUM

DATE: January 11, 1984

TO: Air Oxidation Processes CTG File

FROM: Richard F. Pandullo

SUBJECT: Analysis of Plants With the Potential to Apply Process Modifications to Raise their Cost-Effectiveness Values Above the RACT Cutoff Point

INTRODUCTION

This memorandum describes an analysis performed to identify plants with the potential of applying process modifications to raise their cost-effectiveness values above the Reasonably Available Control Technology (RACT) cutoff outlined in the Air Oxidation Processes Control Techniques Guidelines (CTG) document. The $1600/Mg ($ 1980) RACT cutoff level is associated with a total resource effectiveness (TRE) value of 2.9. In areas where the RACT guidelines are adopted, plants which have a TRE value below the cutoff may opt to upgrade existing recovery equipment or add recovery equipment to raise their TRE values and avoid the incineration requirement. This analysis estimates the potential number of cases for which this option may be applied and describes qualitatively the recovery changes that may be implemented if this option is applied. This analysis does not investigate potential process changes (e.g., changing physical reaction conditions, changing feedstocks or catalysts) that, if adjusted, could change the TRE value.

A rigorous engineering analysis on individual plants was not performed as detailed information regarding plant operations was in most cases unavailable in the emissions data file. Instead, the best scientific judgement was used on the available data. This data included Houdry data reports, Hydroscience Product Reports on specific chemical processes, and the draft CTG document.

The reactor process vent stream characteristics for all fifty-nine plants from Table B-4 of the draft Air Oxidation CTG document were examined. These data are summarized in Table 1. TRE values were calculated for these plants to identify cases where the value was just below the RACT cutoff point of 2.9. TRE values are summarized in Table 1 and the TRE equation used is presented in Table 2. Plants with TRE values above the cutoff point were eliminated from further analysis because they would not be required to use incineration if the RACT guidelines were adopted. For plants with TRE values below 2.9, the VOC emission reductions needed to raise TRE values to the cutoff point were estimated. Focus was given to those plants where the VOC emission reductions needed to reach the TRE cutoff were low to moderate

(<70 percent). On the basis of data calculated and information gathered, an assessment was made to determine whether process modifications could achieve the calculated VOC emission reductions.

RESULTS

Table 3 presents the results of this analysis. Twenty-four out of the 59 plants examined were estimated to have TRE values above 2.9. These plants were excluded from further analysis because if the RACT guidelines were adopted they would be exempt from the incineration requirement.

Nine plants were estimated to have TRE values below 1.0. Further analysis was not performed on these plants because in such cases a VOC reduction of 80 to 90 percent is required to reach the TRE cutoff point. These emission reductions were considered not likely to occur with modifications to product recovery equipment.

The analysis revealed that the remaining 26 plants had TRE values above 1.0 and below 2.9 In this category, 7 plants currently use incinerators and 9 either have been shut down or have changed processes. These plants were excluded from the list of potential cases for process modifications. It was estimated that two plants presently using water scrubbers (#1007, terephthalic acid; #902, cyclohexanone) require 57 percent and 54 percent reductions to reach the cutoff point. Another cyclohexanone plant (#903) also presently using a water scrubber was estimated to require a 64 percent reduction. This level of emissions reduction is not likely to be achieved because most of the VOC emitted from these three plants is insoluble in water and, thus, would probably not be collected by increasing the efficiency of the water scrubber. One additional terephthalic acid plant (#1004) using carbon adsorption was estimated to require a 39 percent reduction to reach the cutoff level. A model plant for this chemical developed by Hydroscience identifies carbon adsorption as 97 percent efficient for VOC removal at this type of plant.[2] This plant was determined to be a marginal but not likely case because assuming the adsorber already achieves a 97 percent reduction, it is unlikely that an additional 39 percent could be removed at a reasonable cost.[1,3]

Six plants out of 59 surveyed were determined to have the potential for applying process modifications to raise their respective TRE values to the cutoff point. Two formaldehyde plants (#1407 and #1420) using product absorbers with no VOC control were estimated to require a 45 percent VOC reduction. Two additional formaldehyde plants (#1403 and #1404) were estimated to require a 1 percent reduction. The Product Report for formaldehyde manufacturing states that one manufacturer (with the same process characteristics as those for the 4 in question) uses a water scrubber following the product absorber which achieves a 74 percent VOC reduction.[4] It was assumed that these plants could potentially do the same at a substantially lower cost than that which would be associated with adding a thermal incinerator.

One acetic acid plant (#205) using a water scrubber was estimated to require a 51 percent reduction in VOC to reach the cutoff. The acetic acid plant was considered a marginal, but likely case because the vent from this scrubber contains a soluble component (acetaldehyde) which is present at a much higher concentration than the non-soluble component.[5] Therefore, modifications to the scrubber to increase efficiency (e.g., addition of scrubber plates) could potentially reduce this soluble component by the required amount.

One final case where process modification could potentially be applied is at a teraphthalic acid plant (#1005) using absorption as a product recovery method. It was estimated that a 20 percent VOC emission reduction is required to increase the TRE to 2.9. It was assumed that this plant could achieve the reduction because a manufacturer using the same process and control was found to achieve an additional 36 percent VOC reduction by adding plates to the existing absorber.[2]

SUMMARY

Absorbers are primarily used as product recovery devices, but can be applied for the purposes of VOC control. In this analysis, it was determined that four plants could potentially add an absorber (water scrubber) and 2 plants could modify existing absorbers to achieve the necessary VOC reduction. Modification of an absorber is commonly done by increasing the size, decreasing the operating temperature, or increasing the number of plates in a column.[2,8]

It was assumed that a plant manager would decide whether to upgrade recovery equipment based on the fact that the alternative control measure would be thermal incineration. In general, the capital and annualized costs, energy requirements, and siting problems would be less significant for upgrading recovery equipment than for applying thermal incineration. In the latter case, equipment is more complex and expensive, fuel requirements and other operating costs are higher, and precautionary siting measures to avoid explosion and fires are more restrictive.[7] The reason for the precautionary measures is that an incinerator has to be situated far enough away from other equipment in the plant so that leakages will not introduce volatile compounds into the vicinity of the incinerator and thereby increase the potential for explosions or fires. Thus, more ductwork is required and greater energy inputs are necessary to route offgas to the incinerator. In addition to the aforementioned relative advantages of upgrading recovery equipment over applying thermal incineration, there is another positive aspect associated with the former. Upgrading recovery equipment can result in an economic benefit by increasing the amount of raw materials, products, and by-products recovered.

TABLE 1. EMISSIONS AND COST EFFECTIVENESS DATA FOR PLANTS

Plant Number	Hourly Emissions (Kg/hr)	Net Heating Value (MJ/Nm^3)	Offgas Flowrate (Nm^3/min)	TRE	Cost Effectiveness[a] ($/Mg)
5102	2150	1.71	1280	0.19	106
904	407	1.63	235	0.32	178
1305	666	1.13	493	0.43	240
1411	357	3.05	510	0.48	268
5101	1370	1.12	1330	0.49	273
1303	326	0.635	430	0.52	290
5201	616	4.56	269	0.60	334
5203	433	2.13	113	0.70	390
5103	895	0.781	1420	0.96	535
5104[d]	1210	0.725	1950	1.02[e]	568
903	103	0.465	170	1.03[e]	574
1807[d]	355	0.808	566	1.06[e]	591
5204[d]	348	2.84	201	1.17[e]	652
1007	223	0.165	527	1.25[e]	697
902	80.2	0.472	170	1.33[e]	741
205[c]	75.0	0.251	142	1.42[e]	791
1306[d]	115	0.535	181	1.49[e]	830
1801[d]	529	0.419	2110	1.53[e]	853
1407[c]	33.7	2.82	56.5	1.58[e]	880
5207[b]	464	0.825	283	1.58[e]	880
2203[b]	155	0.233	481	1.61[e]	897
5208[b]	371	0.825	226	1.63[e]	908
1420[c]	31.4	2.76	56.6	1.69[e]	942
1004	323	0.289	1420	1.77[e]	986
1803[d]	205	0.415	1190	2.17[e]	1,209
1802[d]	211	0.360	1250	2.27[e]	1,265
1005[c]	188	0.153	912	2.32[e]	1,293
2303[b]	617	0.099	3310	2.52[e]	1,404
2302[b]	203	0.154	1130	2.57[e]	1,432
2308[b]	219	0.157	1230	2.58[e]	1,438
1806[d]	135	0.359	850	2.61[e]	1,455
1404[c]	20.3	2.63	67.9	2.71[e]	1,510
5209[b]	78.9	0.825	48.1	2.73[e]	1,521
1804[d]	136	0.483	481	2.82[e]	1,574
1403[c]	15.1	2.82	22.7	2.82[e]	1,574

TABLE 1. (CONTINUED)

Plant Number	Hourly Emissions (Kg/hr)	Net Heating Value (MJ/Nm^3)	Offgas Flowrate (Nm^3/min)	TRE	Cost Effectiveness[a] ($/Mg)
2305	340	0.097	2150	3.03	1,689
5206	125	0.775	133	3.05	1,700
2301	117	0.150	736	3.12	1,739
1422	23.3	0.321	93.4	3.58	1,995
1408	14.6	2.72	70.3	3.89	2,169
1416	39.6	0.114	164	3.92	2,185
2206	36.0	0.093	215	4.16	2,318
5205	228	2.15	603	4.46	2,486
1423	19.5	0.148	110	4.97	2,769
1410	15.8	2.71	161	5.23	2,917
5202	80.2	0.807	170	5.64	3,143
2208	14.6	0.117	90.6	6.02	3,355
1421	16.0	0.148	110	6.06	3,375
2205	27.9	0.070	289	6.66	3,712
1001	78.7	0.393	1530	8.02	4,470
1601	55.0	3.55	1520	8.43	4,698
2204	26.4	0.067	425	9.44	5,259
2207	13.7	0.070	142	10.43	5,815
102	13.7	0.010	340	15.8	8,816
1805	14.1	0.220	1220	37.7	21,000
1601	0.217	1.83	184	443	247,000
1307	2.12	0.001	2830	669	373,000
1409	0.025	2.95	31.1	1814	1,010,000
1418	0.0205	2.56	25.5	2125	1,184,000

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[a] Cost-Effectiveness in $ 1980 (see page 5-25, draft Air Oxidation CTG document).

[b] Incineration is employed to control VOC (only determined for plants marked with (e)).

[c] Possible case for applying process modifications to raise TRE to cutoff point.

[d] Process has been shut down or changed (only determined for plants marked with (e)).

[e] Plant was consided for expanded analysis to determine whether possible case for applying process modifications (i.e., Houdry data, Hydroscience Product Report, and SRI directory were examined).

TABLE 2. EQUATION FOR CALCULATING TRE VALUES

$$TRE = \frac{1}{E}\left[a + b(Flow)^{0.88} + c(Flow) + d(Flow)\,H_T + e(Flow)^{0.88}\,(H_T)^{0.88} + f(H_T)^{0.88}\right]$$

where:

E = emissions, (kg/hr)

Flow = offgas flowrate, (Nm^3/min)

H_T = net heating value, (MJ/Nm^3)

a,b,c,d,e = constants from Table 5-12, draft air oxidation CTG document

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TABLE 3. SUMMARY OF RESULTS FOR 59 PLANTS EXAMINED

No. Plants	Category	Remarks
24	TRE > 2.9	Excluded from further analysis because are already exempt from incineration requirement.
9	TRE < 1.0	Excluded from further analysis because plants require 80 to 90 percent reductions to raise TRE values to cutoff point.
26	1.0 < TRE < 2.9	Considered for expanded analysis because plants require relatively small VOC reductions to raise TRE values to cutoff point. Sixteen (16) plants use incinerators, have been shut down, or have changed processes. Plants using incinerators were excluded because it was assumed they were already affected by another regulation. Two (2) plants (#1007, terephthalic acid and #902, cyclohexanone) use water scrubbers and require approximately 55 percent reductions to attain the TRE cutoff point. Another cyclohexanone plant (#903) using a water scrubber requires a 64 percent reduction. These were excluded because most VOC emitted from these plants is insoluble and would probably not be collected. One (1) terephthalic acid plant (#1004) uses carbon adsorption to achieve a 97 percent VOC reduction (based on model plant); this plant needed a 39 percent reduction to reach the cutoff point. It was deemed unlikely that an additional 39 percent could be attained at a reasonable cost.

TABLE 3. SUMMARY OF 59 PLANTS FROM PROFILE (Continued)

No. Plants	Category	Remarks
	1.0 < TRE <2.9	Two (2) formaldehyde plants (#1407 and #1420) using product absorbers with no additional VOC control were estimated to require a 45 percent VOC reduction to reach the cutoff point. Two (2) other formaldehyde plants (#1403 and #1404) were estimated to require a 1 percent reduction. The formaldehyde product report states that one manufacturer uses a water scrubber following the product absorber which achieves a 74 percent VOC reduction. It was assumed that these plants could potentially do the same at a substantially lower cost than that associated with adding a thermal incinerator. One (1) terephthalic acid plant (#1005) using absorption needs a 20 percent VOC reduction to reach the cutoff point. This plant was determined to have the potential for process modifications because a manufacturer in the industry using the same process and control achieved a 36 percent VOC reduction by adding plates in the absorber. One (1) acetic acid plant (#205) uses a water scrubber and needs a 51 percent VOC reduction. This plant was determined to be a marginal, but likely case for process modifications based on the fact that the vent from this scrubber contains a soluble component and the soluble component in the offgas is present at a higher concentration than the non-soluble component.

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7. Radian Corporation, 1978. Control Techniques for Volatile Organic Emissions from Stationary Sources. EPA-450/2-78-022. Emission Standards and Engineering Division. Office of Air Quality Planning and Standards. Research Triangle Park, North Carolina. May 1978.

APPENDIX G: PUBLIC COMMENT LETTERS ON THE DRAFT CTG

CMA

CHEMICAL MANUFACTURERS ASSOCIATION

April 26, 1984

Mr. Robert Rosensteel
Chemicals and Petroleum Branch
Emissions Standards and
Engineering Division (MD-13)
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

Re: CMA informal comments on EPA's Draft Control Techniques Guideline (CTG) Document for control of Volatile Organic Compound Emissions from Air Oxidation Processes in the Synthetic Organic Chemical Manufacturing Industry.

Dear Mr. Rosensteel:

The Chemical Manufacturers Association (CMA), a nonprofit trade association whose member companies represent more than 90% of the production capacity of basic industrial chemicals within this country, submits the following informal comments on EPA's Draft Control Techniques Guidelines (CTG) Document for Control of Volatile Organic Compound Emissions from Air Oxidation Processes in the Synthetic Organic Chemical Manufacturing Industry, 49 Federal Register 8077 (March 5, 1984). Our comments submitted today do not address all the issues covered in this CTG: Therefore, we reserve the right to submit additional comments as part of the future regulatory activity on this matter. These comments were prepared after deliberation and consultation among CMA members.

Many CMA member companies use or anticipate using chemical manufacturing air oxidation unit processes that could be covered by the proposed CTG. Accordingly, CMA has a direct and vital interest in the content of the draft CTG as it will affect the implementation of the proposed Air Oxidation New Source Performance Standard.

To the extent that the draft CTG document establishes a pattern for future EPA control techniques guidelines, CMA is concerned that in numerous respects, as described in the following paragraphs, the draft document is technically unsound. CMA has six principal concerns with the draft CTG:

1. Inadequate general discussion.

The general discussion covering the Air Oxidation Industry is vague. It does not adequately detail what the industry is or where it is. Some of the information that is presented is incorrect and misleading. For example, on page 2-6, Amoco-Standard Oil is listed as manufacturing acetone and phenol. The statement is not correct. Again, on page 2-13, Amoco-Standard Oil is listed as producing acetone and phenol in Richmond, California. Amoco not only does not manufacture these materials, but there is no Amoco-Standard Oil facility in Richmond, California.

The chemicals covered by this CTG have been listed in an inappropriate way. The list is given as not being exclusive. This creates a certain amount of uncertainty as to which chemicals are covered. This ambiguity can be easily taken care of by giving an all-inclusive list for which this CTG applies. This has been done in the past, as in the VOC Equipment Leaks (Fugitives) NSPS. The burden should be on the Agency to declare beforehand what chemicals will be controlled and not for the regulated community to guess whether or not they are covered. On page 3-29, in a discussion of existing state regulations, the document unfortunately misrepresents the regulatory situation in Illinois. In fact, the Illinois rule requires emissions to meet one of three control levels: 1) 8 pounds/hour, 2) 10 ppmv equivalent methane, or 3) 85% destruction. We recommend the Agency clarify these points.

2. Inadequate definition of vents controlled.

The present language in the draft CTG does not clearly indicate which vents are to be controlled. A reactor system may have a bottoms stream which is liquid or solid with entrained air. This stream is processed through product purification operations which may subsequently have a small vent. This CTG was not intended to cover these vents; it was intended to cover vents from the vapor stream of the reactor. The document should be revised to so reflect this point.

The document, as presently written, does not address the situation where the reactor vapor stream is vented from more than one place. For example, the gas may vent through two scrubbers in a series. The vents should be treated separately for calculating the Total Resource Effectiveness (TRE) index. This needs to be clarified; otherwise, highly efficient multi-stage product recovery technologies or control techniques may be unnecessarily discouraged. A similar situation occurs when a side stream is drawn off of the vent for some other purpose, such as use as a conveying gas. The inclusion of vents from other uses could be unrealistically restrictive in calculating the TRE index and prescribing control requirements.

3. Inadequate consideration of alternative control technologies.

The CTG states, "The choice of thermal oxidation as the single control technique for analysis yields conservative estimates of energy, economic, and environmental impacts since thermal oxidation is relatively expensive and energy-intensive." While agreeing with this statement, it is not true that the control efficiency of thermal oxidation is much less dependent on process and waste stream conditions than are other control techniques nor is thermal oxidation economically applicable to all Synthetic Organic Chemical Manufacturing Industry (SOCMI) air oxidation processes. Destruction efficiency will depend on flame stability which, in turn, depends on composition, heating value and flow rate of the waste stream. Variations in these must be taken care of with auxiliary fuel. Some process conditions will not lend themselves to efficient operation of thermal oxidation and, therefore, other control techniques should be used and encouraged. The draft CTG does not adequately address alternative technology strategies which might be more effective; we strongly recommend the draft CTG be modified to address this matter.

4. Unrealistic economic considerations.

The economic impact of emission controls are underestimated. First, the draft CTG ignores the costs of siting, utilities, services, connections and R&D. The addition of a thermal oxidizer to an existing facility can sometimes be facilitated by using existing services. However, many times the unit must be placed at some distance from the vent source and requires considerable expenditure for siting, utilities and connections. The cost summary also assumes that the disposal cost of NaCl from scrubbers is insignificant. If the disposal is even possible, a discharge permit is generally required which will require monitoring and control for pH, total dissolved solids (TDS) and organics. The cost of such treatment and disposal is not insignificant. The analysis also assumes a substantial energy credit in many cases. In many processes, especially halogenation, energy recovery is not feasible. In other processes where energy can be recovered as steam, the steam generated would be low pressure steam which may have no economical use within the process. For these reasons, the costs associated with thermal oxidation have been understated. It will cost considerably more than the EPA estimate to accomplish the emission reductions proposed in this document. We recommend EPA reconsider these economic costs and correct the CTG.

5. Unclear use of TRE cutoff.

We strongly support the concept of using the TRE index for defining appropriate control technology. Nevertheless, additional clarification is needed. Examples and explanations of how to use and apply the TRE need to be included. On page 5-26, it should be clarified that "E" (hourly emissions) is just the VOC emissions and "Flow" is the total flow of the vent stream.

On page D-1, the document states that reasonably available control technology (RACT) requires no additional control in a situation where the TRE is greater than 2.9. Then on page E-2, in a discussion of the TRE, the cutoff if given as 1.0. This is confusing. A TRE cutoff calculation is a reasonable approach to evaluating alternative control techniques and determining if control is necessary. CMA recommends that the draft CTG be clarified as to the intended use of the TRE Index and identify the " no additional control" RACT cutoff.

6. Typographical error on Page E-3.

It appears there is a typographical error on page E-3. We believe that line A2. should read:

" For Chlorinated Process Vent Streams, if 3.5   Net Heating Value (MJ/Nm^3)."

We submit these comments for your serious consideration and appropriate revision and development of a revised "CTG for Control of Volatile Organic Compound Emissions from Air Oxidation Processes In the Synthetic Organic Chemical Manufacturing Industry." We would be pleased to discuss our informal comments with the Agency's personnel or furnish further supporting data. For additional information, please do not hesitate to call me at (202)887-1178.

Sincerely yours,

Robert R. Romano

Robert R. Romano, Ph.D.
Manager - Air Programs

Diamond Shamrock
Chemicals Company

Gulf Coast Area

April 18, 1984

Mr. Robert Rosensteel
Emissions Standards and Engineering Division (MD-13)
Environmental Protection Agency
Research Triangle Park, North Carolina 27711

RE: Draft Control Techniques
Guideline (CTG)
Air Oxidation Processes in the SOCMI

Dear Mr. Rosensteel:

The attached are comments submitted by Diamond Shamrock Chemicals Company on the above referenced draft CTG. We appreciate the opportunity to review this document. We hope that our comments will be carefully considered and acted on by your office. Should you have any questions on our submission, please contact me at (713) 476-1247 or the letterhead address.

Sincerely,

Mel Skaggs/bh
M. M. Skaggs, Jr., P.E.
Senior Environmental Engineer

MMS/bh
Attachment

Diamond Shamrock Chemicals Company A Subsidiary of Diamond Shamrock
1149 Ellsworth Drive, Pasadena, Texas 77501 Phone 713 476-2000

COMMENTS ON MARCH, 1984 DRAFT DOCUMENT ENTITLED "CONTROL OF VOLATILE ORGANIC COMPOUND EMISSIONS FROM AIR OXIDATION PROCESSES IN SYNTHETIC ORGANIC MANUFACTURING INDUSTRY"

Diamond Shamrock Chemicals Company (DSCC), a wholly owned subsidiary of the Diamond Shamrock Corporation, owns and operates 29 domestic plants in 10 states. One of these plants is an oxyhydrochlorination plant producing 1,2-dichloroethane (EDC) in Deer Park, Texas. These comments are submitted because of the impact that this draft CTG could have on our Deer Park operations. The comments made below are divided into two sections - Technical Comments and Cost Analysis.

DSCC supports the concept of using sound technical data in the development of these CTG's, as well as the use of cost effectiveness indexing, in determining when they should be applied. To this end, we complement the technical work done to date on this document and on the development of the TRE concept. We believe it is imperative that, where the EPA is formulating major new VOC emissions reductions, the EPA should also provide the technical means to obtain these reductions. The result otherwise will be (and has been) inequitable across-the-board required reductions, which generate widely varying costs per ton in the different affected industries and facilities.

It is with some regret, therefore, that we must raise several serious objections to this draft document. At least two viable control schemes were either omitted or not seriously considered in drafting this document. In addition, the proposed TRE scheme suffers from both theoretical and empirical flaws. These two areas of deficiency form the bulk of our comments on this proposal. They should be seriously addressed and undergo additional public review before the CTG is finalized.

Technical Comments

1. A 95% control efficiency should be adopted as RACT.

This draft document proposes to use 98% as the control efficiency which qualifies as R.A.C.T. This figure was selected because it seems to be achievable in all conventionally fired vent gas incinerators. The reason why 98% was selected over some nominally lesser figure (such as 95%) was not stated. If a slightly lower figure was selected instead, the regulated companies would have a choice of three acceptable control schemes instead of only one. These three options would include thermal oxidation, catalytic incineration, and flares. The 95% figure suggested in our comments should be reviewed by EPA and revised up or down in such a way as to include all three technologies.

We recommend that the EPA choose a figure such as 95% as the selected RACT control efficiency. Such a revision would allow the affected companies to choose between the alternatives based on a proper blend of capital availability, operating costs, and process requirements. Allowing a wider choice of control alternatives would allow more facilities to meet the less than $1,600/Mg. criteria. Since more facilities probably would be installing controls, greater emissions reductions would result. Thus, selecting a 95% cut-off figure would be better for both the regulated community and the regulators.

2. Flares should be included as one of the control measures.
Flares are a very economical and efficient means of controlling off-gas vent emissions of hydrocarbons. Recent work conducted by the EPA and CMA have demonstrated the high organic destruction efficiencies of flares. Flares are much less expensive to construct and maintain than are "thermal oxidation" units (incinerators). It makes little sense, if a flare may be erected for $100,000 and produce a 95% control efficiency, to require a $5,000,000 incinerator to be installed in order to achieve a 98% efficiency. The last 3% of reductions come at an extremely high price. As our comments below explain, such alternative control schemes should be compared to determine the cost per additional ton removed.

3. Catalytic Incinerators Should Qualify as RACT.
The development of effective catalytic incineration technology during the mid-to-late 1970's was a very important technological advancement. This technology allowed vent gases to be efficiently destructed at one-third or less of the energy input necessary for thermal incineration. The text of the subject draft makes it appear that the 98% figure was selected specifically to exclude catalytic incineration. The additional 1 - 3% removal efficiency provided by thermal incineration is only achieved at the expense of large quantities of energy consumption. This decision seems to be totally at odds with a national energy policy which spends over $40 billion/year attempting to conserve energy (DOE).

The emission reductions represented by 98% (over 95%) efficiency are not likely to result in any detectible environmental benefits. Since the "low cost" gas of the past is no longer available, at least some of the newly constructed thermal incinerators will burn either fuel oil or coal. The SO_2, NO_x, and particulate emissions from these units are likely to be quite large compared to this 1 - 3% VOC reduction. If only a few of these units could be encouraged to use catalytic incineration (over thermal incineration), some quite measurable environmental impacts may be avoided. We believe that the EPA should be encouraging, not discouraging, catalytic incineration.

4. OHC-EDC plants should not be included in this CTG.

We fail to understand why OHC-EDC plants are to be regulated under this CTG. The chlorinated solvent industry presents fundamentally different vent control problems from other non-halogenated processes noted. Additionally, all but two of the affected EDC plants are presently located in Texas and Louisiana, where vent incineration is already required (per this Draft). One of the other two plants is located in California and is already subject to very stringent regulation. We believe that the lone remaining facility in Kentucky would best be addressed through that State's SIP process (if there is environmental cause to do so).

5. NO_x Emissions from coal combustion are independent of fuel nitrogen.

NO_x Emissions from coal combustion are erroneously attributed to fuel nitrogen content on Page A-21. These emissions are conventionally thought of as being independent of fuel nitrogen. Technical literature as recent as August, 1982 provides support for the AP-42 position (see "A Promising NO_x-Control Technology", Environmental Progress, August, 1982, Page 167-177). If the EPA has new data which revises this position, DSCC would be most interested in reviewing it.

6. Gross omissions exist at Page 3-18.

Material was omitted from this draft in the catalytic incineration section (Pages 3-17 to 3-19). Since this section was of primary importance to DSCC, we request that we be sent a revised copy of this document and that the comment period be reopened to allow review of this section. The nature of the omission makes it impossible for us to speculate how much material was omitted. The fact that the pages are sequentially numbered (without any numbers being missing) indicates that everyone reviewing this document were unable to review this important section.

7. Table 2-6 contains inaccurate information.

Diamond Shamrock Corporation sold its La Porte, Texas EDC/VCM facility to B. F. Goodrich Corporation during 1981. Please correct this entry, as well as the corporate name (to Diamond Shamrock Chemicals Company) of our Deer Park Plant.

8. The Draft document provides conflicting TRE index cutoff values.

The Draft document states, in Section 5 and Appendix E, that all plants with a TRE index less than 1.0 would be required to install RACT. Appendix D states that this cut-off value will be 2.9. We are unable to resolve this discrepancy, but we feel that any control costs beyond the presently proposed $1,600/Mg. would be excessive.

Cost Effectiveness Comments

The Index formula, as proposed, is fatally flawed.

DSCC strongly supports the concept of selecting national and state air emissions control regulations based on cost impact. A cost per unit of production scheme would certainly seem to be the most equitable means of analyzing air pollution control strategies. Such a scheme would allow a clear examination of the resources being invested in controlling these emissions. Costs incurred in controlling emissions are passed on to the consumers. A cost per unit of production guideline would present such regulations in their true light - they are a tax on the consumer. Short of the adoption of this alternative approach, regulations should be based on a cost per ton of additional pollutant removed.

The TRE approach seems to be a plausible means of assessing the cost effectiveness of the proposed controls. As presented in this draft, however, the TRE has four significant flaws. These flaws include outdated costs, a lack of flexibility, ignored expenses, and an inability to look at the incremental cost aspects of the alternatives. These concerns are discussed below.

1. Out-of-Date Costs

The cost factors used in this proposed formula have not been examined in five years (although they were uniformly inflated to 1980 levels). The market forces of the past five years have been unparalleled in our country's history. Adopting a CTG based on such outdated costs is poor scientific and technical practice. The formula should be revised to allow the use of the present and reasonably projectable future costs, based on the date of application.

2. The TRE formula is unacceptably inflexible.

The TRE formula also erroneously assumes that labor and energy costs are uniform nationwide. It seems indefensible to require a company to calculate their "control costs" based on $11.10/hour wages and $2.40/MCF gas prices when they are actually paying $18.00/hour and $5.67/MCF. Energy, labor, and electricity costs all probably vary by a factor of at least two fold within the EDC producers group alone. The use of the TRE formula should be revised to allow a company to use its true costs. If the regulation is intended to measure the "cost effectiveness" of the regulation, the TRE formula must be changed in this way.

3. The TRE index formula simply ignores several expenses.

The TRE index ignores or virtually ignores several costs. These significant costs should be included in the revised CTG. These costs include the following:

a) Wastewater treatment expenses (steam, neutralization expenses, equipment, labor, etc.);

b) Carbon steel could not reasonably be used in the majority of the affected EDC plants;

c) Heat recovery unit downtime (15%);

d) Maintenance costs (should be at least 10% per year).

e) Operating Supplies (20% of operating labor);

f) Laboratory Expenses (15% of operating labor; and

g) Utility hookup, site development, process connection piping, and land costs.

These costs should be included in the final TRE formula.

4. Incremental Cost Effectiveness

The TRE formula fails to examine the cost effectiveness problem from a logical standpoint. To look at cost effectiveness correctly, one must compare the cost required to remove the last ton of a pollutant as well as the average cost per ton (present proposal). This problem can best be understood by looking at the following example. 1) Assume that control Strategy A will remove 95% of a 1,000 TPY VOC source's emissions at a cost of $475,000 per year. Thus, Strategy A has a cost per ton removed of $500/ton and removes 950 TPY. 2) Assume that control Strategy B removes 98% of a 1000 TPY source at a cost of $1,500,000 per year. Thus, Strategy B has a cost per ton removed of $1,520 (removes 980 TPY) and also easily falls within the CTG. 3) Note, however, that the last 30 TPY were removed at a cost of $1,025,000 per year, or at a cost of $34,167 per ton!

The above example demonstrates the problems associated with not comparing incremental control costs of the various control schemes. The removal of the last 30 tons is obviously a very poor investment of resources, and is unlikely to contribute to any discernable environmental improvement. The above example shows precisely why catalytic incineration should be re-examined as being RACT, and why we support the use of a 95% or similar technically supportable control limit.

Summary

DSCC strongly supports the development of cost-based air pollution control regulations, but we are just as strongly opposed to the use of faulty "cost effectiveness" evaluation procedures. We request an impartial review of the data in this Draft CTG and in other EPA air programs offices from an incremental cost standpoint. We believe that once these economics are re-examined, it will be obvious that the cost of going from a 95% to a 98% control efficiency is extremely high. We, therefore, request that RACT be set at a level that will allow catalytic incinerators and flares to also be considered. Such a level would allow impacted companies to select the control method best (most economically) suited to their operational setting. By allowing the use of the strategy best fitted to individual operations, the EPA should reduce the number of companies avoiding control through the TRE escape formula. Such an approach might also avoid some of the SO_2, NO_x, and TSP emissions which will result from thermal incineration by allowing the use of catalytic controls.

ETHYL CORPORATION

CORPORATE ENVIRONMENTAL AFFAIRS

PLEASE ADDRESS REPLY
TO: P. O. BOX 341
BATON ROUGE, LA. 70821

March 28, 1984

Emission Standards and Engineering Division (MD-13)
Environmental Protection Agency
Research Triangle Park, North Carolina 27711

Re: Guideline Series -- Control of Volatile Compound Emissions from Air Oxidation Processes in Synthetic Organic Chemical Manufacturing Industries Draft Document

Attention: Mr. Robert Rosensteel:

Dear Mr. Rosensteel:

This document lists two Ethyl facilities in Table 2-6, page 2-18, as manufacturing sites for 1,2 Dichloroethane by the air oxidation process. This is incorrect.

In January, 1983, the 1,2 dichloroethane air oxidation process unit in Baton Rouge, Louisiana was shut down. The manufacture of 1,2 dichloroethane at Pasadena, Texas does not employ air oxidation and uses alternative technology.

Please incorporate these changes in future revisions of the document.

Sincerely,

D. E. Park

D. E. Park, Director

DEP:jtd

cc: J. W. Parson
W. P. Gafford

Standard Oil Company (Indiana)
200 East Randolph Drive
Chicago, Illinois 60601
312-856-2506

J. D. Reed
General Manager, Environmental
Affairs & Safety

April 19, 1984

Emission Standards and Engineering Division (MD-13)
Environmental Protection Agency
Research Triangle Park, NC 27711
Attention: Mr. Robert Rosensteel

Sir:

Control Techniques Guideline Document; Air Oxidation Processes in the Synthetic Organic Chemical Manufacturing Industry; Draft Document for Public Review;
49 Federal Register 8077, March 5, 1984

Standard Oil Company (Indiana), on behalf of its Amoco subsidiaries, appreciates this opportunity to comment on the draft Control Techniques Guideline Document for volatile organic compound emissions from air oxidation processes in the synthetic organic chemical manufacturing industry. As indicated in the Federal Register notice, Control Technique Guideline (CTG) Documents are meant as informational material for use by the states in determining the appropriate controls for various stationary sources in nonattainment areas. Both the states and industry use these documents to determine which sources are subject to control under an emissions reduction program. Therefore, the documents must be accurate and clear. Our review has shown this document to be deficient in both these areas.

This CTG focuses on the volatile organic compound control techniques for air oxidation unit process vents in the synthetic organic chemical manufacturing industry, and concludes that thermal oxidation is the only demonstrated technology universally applicable. In this analysis, the document never fully explains the scope of the potential regulation. Neither the chemicals produced by the air oxidation process nor the emission points potentially subject to control are clearly enumerated. The published list of chemicals (page 2-2) is described as "not exclusive." Thus, if a plant does not produce any chemical on the list, it cannot be certain that it is not covered. In addition, the description of the industry which does appear in the document is not completely accurate. For example, "Amoco-Standard Oil" is listed as a producer of acetone (page 2-6). In fact, Amoco does not have any plants which produce acetone. In view of these deficiencies, the CTG cannot be considered effective guidance for the states. We suggest that EPA include a list of chemicals, similar to that published for the New Source Performance Standards from SOCMI Distillation Units (48 Federal Register 57538), in the final guidance document.

As described in this document, the need for application of thermal oxidation technology to process vents is determined by the associated total resource-effectiveness index (TRE) calculated for a given unit. That is, thermal oxidation is recommended only where the process flowrate, VOC emissions, corrosion properties, net heating value, and economics combine to make its application "reasonable." However, the document fails to clarify the vents for which this calculation should be made. For example, Figure 2-2 (page 2-31) illustrates a vapor phase air oxidation process. There appear to be two vents for gases leaving the unit: one described as "off gas" and one from the product purification section. From discussions with the Agency, we understand that the vent from the product purification step would not be covered by this regulation. However, the CTG itself does not make this differentiation of vents clear.

This lack of clarity is further compounded by multiple-step process stream vents. For example, off gas is frequently split at the end of a unit process. Some gas passes through a scrubber and is vented. The other portion is used as a carrier gas, and passes through to a storage vessel and scrubber before venting. Thus, there are essentially two vents for one process stream. These atmospheric vents either could be calculated individually and added together or could be calculated as a unit by adding the flowrates, emissions, and heating values before application of the TRE equation. Again, although discussions with the Agency have led us to believe that the vents should be calculated individually, we can find no justification for this in the document. We urge EPA to clarify the means for application of the TRE calculation in the final CTG document.

In conclusion, Standard Oil Company (Indiana) believes the CTG document for VOC emissions from air oxidation processes does not provide adequate guidance for states to use in developing their control strategies. Furthermore, our analysis of the data indicates that fewer than 25 plants have the potential to be controlled more effectively under the CTG guidelines than under present controls. We, therefore, question the need for this particular CTG and suggest the Agency concentrate its resources on developing regulations with more potential benefit.

Sincerely,

JDReed

J. D. Reed

CEC/ts

TCC TEXAS CHEMICAL COUNCIL
1000 BRAZOS, SUITE 200, AUSTIN, TEXAS 78701-2476, (512) 477-4465

April 9, 1984

EMISSION STANDARDS AND ENGINEERING DIVISION (MD-13)
U. S. ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, N.C. 27711

ATTN: MR. ROBERT ROSENSTEEL

RE: COMMENT ON THE DRAFT CTG DOCUMENT, AIR OXIDATION PROCESSES IN THE SYNTHETIC ORGANIC CHEMICAL MANUFACTURING INDUSTRY

Dear Mr. Rosensteel:

Because there was a couple weeks delay in getting copies of the subject CTG from the Library, Texas Chemical Council (TCC) member companies are late in reviewing and getting comments in for submittal to the EPA. TCC requests an extension until May 1st for the submission of comments.

Thank you,

Andy Nickolaus

A. H. Nickolaus
Chairman, CTG Subcommittee

cc: J. B. Cox - Exxon
R. R. Romano - CMA

AHN/cgh

TEXAS CHEMICAL COUNCIL
1000 BRAZOS, SUITE 200, AUSTIN, TEXAS 78701-2476, (512) 477-4465

April 24, 1984

EMISSION STANDARDS & ENGINEERING DIVISION (MD-13)
ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, N.C. 27711

Attn: Mr. Robert Rosensteel (2)

RE: Comments on the Draft CTG;
Air Oxidation Processes

Dear Mr. Rosensteel:

Attached are comments by the Texas Chemical Council on the subject Control Technique Guideline.

Sincerely yours,

Andy Nickolaus

A. H. Nickolaus
Chairman, CTG Subcommittee

cc: J. B. Cox - Exxon
T. E. Lingafelter - Dow
R. R. Romano - CMA
TCC Files

AHN/cgh
Attachment

COMMENTS BY THE TEXAS CHEMICAL COUNCIL ON THE DRAFT CONTROL TECHNIQUE GUIDELINE (CTG) FOR CONTROL OF VOLATILE ORGANIC EMISSIONS FROM AIR OXIDATION PROCESSES IN THE SYNTHETIC ORGANIC CHEMICAL MANUFACTURING INDUSTRY (SOCMI), MARCH, 1984

The Texas Chemical Council (TCC) is an association of 83 chemical companies having more than 70,000 employees in Texas and representing approximately 90% of the chemical industry in the State. Over 25% of the nation's air oxidation plants are located in Texas so the proposed CTG is of vital concern to us.

I. Concerns

The TCC's major concerns are:

- The draft CTG does not fulfill its stated purpose (page 1-1) of providing "State and local air pollution control agencies with an initial information base for proceeding with their own analysis of Reasonably Available Control Technology (RACT) for specific stationary sources" (underlining added). No basis for the determination of RACT is given. Instead RACT requirements are dictated without explanation in Chapter 4.

- The $1,600/Mg annual cost cutoff ($1,450/ton) is excessively expensive and, on the average, exceeds the cost of supposedly more stringent New Source Performance Standards (NSPS).

- The cost cutoff is understated. It is in June, 1980 dollars and is equivalent to $1,970/Mg today. Further, costs are underestimated. The Total Resources Effectiveness (TRE) calculation ignores items of appreciable cost so that it underestimates actual costs by 50%. TCC estimates the actual cutoff cost in current dollars to be $2,950/Mg.

- There are inexplicable inconsistencies between the factors used for the TRE calculation in this CTG and those used in the recently proposed Air Oxidation NSPS (Reference 1).

II. Recommendations

- EPA should explain how they arrived at their RACT definition and provide more guidance to states on how they expect them to apply it to individual situations.
- An annual cutoff cost in the range of $500/Mg in current dollars is recommended as being consistent with existing State Implementation Plans and average NSPS costs.
- The TRE calculation should include the cost elements discussed in Section III C.
- The factors used in the CTG and NSPS TRE calculation should be consistent. TCC recommends the factors from Table 8-3 of the Polymer/Resin NSPS (Reference 8).

III. Discussion

A. The Draft CTG Does Not Fulfill Its Stated Purpose.

After noting that State Implementation Plans (SIPs) must include RACT, the introduction to the CTG states (page 1-1) that "the purpose of CTG documents is to provide State and local air pollution control agencies with an initial information base for proceeding with their own assessment of RACT for specific stationary sources" (underlining added). The CTG does not do this. Instead, RACT requirements are dictated without explanation in Chapter 4. No basis is given there for the definition of RACT, what alternatives, if any, were considered is not mentioned, what cost guidelines were followed is not explained, and no guidance useful to "State and local air pollution control agencies ... for proceeding with their own analysis of RACT ..." is supplied. Further, it's virtually impossible for a State to show that any differing state regulation is within 5% of EPA's RACT which, we understand, was required for the 1979 SIPs. Thus the EPA is, in effect, rule-making without going through the rule-making process.

B. The $1,600/Mg Cutoff ($1,970/Mg In Current Dollars) Is Too High.

EPA has used a $1,600/Mg cutoff in June, 1980 dollars as the annual abatement cost which is equivalent to a TRE Index of 1.0. Thus, using the standardized TRE cost calculation, any vent stream with an annual abatement cost less than $1,600/Mg (June, 1980 dollars) must be abated. This cost is too high.

1. What Kind Of Dollars Is EPA Talking About?

Clarification of what kind of dollars the EPA is talking about is needed before discussing why their cutoff figure is too high. The dollars in this CTG are June, 1980 dollars. This is not made clear in the text and is misleading since the normal presumption in the absence of a specific note is that the dollars are current with the publication date. Using the implicit GNP deflator, $1,600/Mg in June, 1980 becomes about $1,970/Mg now. An appreciable difference!

2. Why A Cutoff Of $1,600 (June '80$)/Mg Is Too High.

In discussing the cutoff for the Air Oxidation NSPS (Reference 3) EPA admits that "in prior source categories for which NSPS have been developed, VOC maximum estimated control costs have generally not exceeded $1,000 per megagram." Why then is EPA proposing a CTG that is more costly than supposedly more stringent New Source Performance Standards? In the Air Oxidation NSPS EPA felt obligated to justify their proposed cutoff figure. Surely they owe the public as much here. Incidentally, TCC found EPA's NSPS explanation totally unconvincing as was explained by our comments in Reference 4.

The $1,600/Mg figure is also out of line with present State RACT regulations. In 1982 Texas had to revise their ozone SIP for Harris County to provide additional reduction of Volatile Organic Compound (VOC) emissions. They first prepared a list of emitting sources, next they estimated abatement costs (Reference 2), and then regulated those with the lowest cost. Additional regulations for the chemical industry were in the $200-$300/ton range with the highest being $832/ton for vents from carbon black manufacturing - a maximum equivalent to $810/Mg in June, 1980 dollars.

C. The TRE Calculation Underestimates Actual Costs

The TRE calculation ignores capital and annual items of appreciable cost so that it underestimates actual costs.

1. Capital Costs

EPA's estimates of capital costs appear to be reasonable for those elements they cover. It's those they don't that make their estimates less than actual in many cases. Page 5-9 of the CTG states that EPA's costs "do not include the provisions for bringing utilities, services, or roads to the site, the backup facilities, the land, ... or the process piping and instrumentation interconnections that may be required within the process generating the waste gas feed to the thermal oxidizer." Yet all these facilities, and others, are required to make a system that will operate.

TCC compared capital costs for actual flare systems against those estimated by the EPA in the preliminary draft Polymer/Resin NSPS (Reference 5) and found that EPA's estimates for intermediate sized systems were about 25% low. Simarily, piping costs on a comparable basis were 12% to 25% below actual. TCC noted in these comparisons the importance of items not included in the estimate. Then on March 9, 1984, as part of their comments (Reference 6) on the proposed Distillation Unit Operations NSPS, TCC provided a detailed estimate for a flare system for one of EPA's sample cases. TCC's estimate compared to EPA's was:

	M$ (1st Qtr. 1984)	
	TCC	EPA*
Flare	55	40
Piping	145	72.5
Necessary Items Not Included by EPA	188	0
Total	388	112.5

* Costs escalated from CE Fabricated Equipment Index of 244 in 1978 to estimated 331 in 1st Quarter 1984.

The magnitude of necessary items not included in EPA's estimate is disturbing. Time and the absence of design algorithms in this CTG have prevented the TCC from making a similar estimate and comparison for thermal incinerators, but such an independent estimate needs to be made. We urge the EPA to have the example case in Appendix E estimated by a large construction firm that both designs and builds chemical plants. The estimate should include all those elements that are necessary to make the system operable.

In their estimate, EPA allows for only 150 feet of ductwork between the source and the thermal oxidizer. TCC believes costs should be estimated based on 300 to 500 feet of ductwork with pipe bridge. On June 1, 1974, an explosion occurred at a chemical plant in Flixborough, England, killing 28 people and causing over 80 million dollars in damage. It was caused by leakage of cyclohexane vapors from an oxidation unit and their subsequent ignition by a source some distance away. The potential for such a massive explosion from this type of process had not been fully appreciated by the chemical industry. As a result, many owners would be unwilling to locate an ignition source as large as an incinerator as close to process buildings as 150 feet. Thus 300-500 feet would be a more representative figure.

2. Annual Costs

EPA ignores several items of appreciable cost in its estimate of annual costs. These include: operating supplies, laboratory costs, engineering/environmental oversight, and some general plant overhead items. A comparison of annual costs as estimated in this CTG and by TCC is given in attached Table 1. Discussion of cost elements not included by EPA is given below.

a. Operating Supplies

In addition to maintenance materials, operating supplies are also necessary. These include such items as charts, lubricants, test chemicals, personal safety equipment, custodial supplies, and similar materials which cannot be considered raw materials or maintenance and repair materials. At one large Texas SOCMI plant these factors ranged from 9-33% of operating labor for six SOCMI processes. For the powerhouse, factors were 15-20% of operating labor over a three year period. See also Reference 7, page 201.

b. Laboratory Expense

Some laboratory expense is incurred by this regulation and needs to be allowed for. Reference 7 recommends 10-20% of operating labor for this.

c. Technical Oversight

It may come as a surprise to the EPA but the Code of Federal Regulations is not widely read by production foremen and supervisors. Thus some environmental/engineering oversight is needed for training, monitoring oversight, filing required reports, technical advice, etc. Total technical costs (mechanical, chemical, environmental, etc.) run over 25% of operating labor for many SOCMI processes.

d. General Plant Overhead

General plant overhead covers a host of operations and services necessary for plant operation and these are estimated in Reference 7 (page 203) to be 50-70% of the total of operating labor plus supervision plus maintenance. Some of these have been detailed above and we presume some others are included in the EPA's 11.10/hour (June, 1980 dollars) labor rate. Remaining unaccounted for plant overhead costs include safety services, plant protection, central machine shops, stores, stenographic and mail services, purchasing, accounting other than payroll, etc.

e. Recommendation

The Petroleum Refining Fugitive BID (Reference 9) adds a 40% of operating and maintenance labor factor to cover administrative and implementation costs. The TCC recommends a similar factor be included here to cover items 'b' through 'd' above.

D. There Are Inexplicable Inconsistencies Between This CTG And The Proposed Air Oxidation NSPS.

The cost basis for both the CTG and NSPS are identical but for the same example vent stream they arrive at different costs.

	Air Oxidation NSPS	Air Oxidation CTG
Cost Effectiveness, $/Mg Cost Base Year	800 Dec. 1978	$1,136 June 1980
Cost Effectiveness, $/Mg Indexed to Current Dollars	1,095 1st Q 1984	$1,400 1st Q 1984

These differences arise from the use of different cost factors in the TRE calculation. The factors are:

	NSPS BID Table 8-7	This CTG Table 5-7	Enviroscience (Reference 10)
Cost Base Year	Dec. 1978	June 1980	Dec. 1979
Operating Labor, $/hr. Includes Overheads?	13.08 Yes	11.10 Yes	$15.00 Not Specified
Electricity, $/KWH	0.02616	0.049	0.03
Natural Gas, $/GJ	4.78	2.40	2.00
Scrubbing Water, $/1000 gal.	0.22	0.79	0.25
Caustic Price, $/lb.	0.0436	0.0563	0.05

Although these are for different base years they cannot be reconciled by any logical indexing scheme. Most are said to have been indexed from Enviroscience data given in Reference 10. These are shown but they don't make things any clearer.

Obviously a consistent set of factors should be used but TCC recommends none of the above. More rational and more soundly based factors are supplied in the Polymer/Resin NSPS (Reference 9) and TCC recommends them. They are:

	Polymer/Resin BID Table 8-3
Cost Base Year	June 1980
Operating Labor (Includes Labor Related Overhead)	$18/Hour
Electricity	$0.049/KWH
Natural Gas	$5.67/GJ ($5.98/MMBTU)
Steam	$13.62/Mg ($6.18/1000 Lb.)
Water Price	$0.079/$M^3$ ($0.30/1000 Gal.)

E. Miscellaneous

1. The CTG uses "Nm^3" for normal cubic meters. This is confusing since "N" is the standard symbol for Newtons, a unit of force, in the International System of Units per the American Society of Testing and Materials "Standard for Metric Practice." TCC recommends this be changed to something like "scm" as was done in the Distillation Operation NSPS.

2. The CTG states that sodium chloride disposal costs are insignificant in almost all existing plants. Maybe that's why they have scrubbers already. But the CTG is not aimed at these. It's for plants that don't have scrubbers. In general the disposal of dilute brine streams is not cheap unless the plant is located near salt water and can get a permit to dump its brine. The Air Oxidation NSPS mentioned deep well disposal as an acceptable means. Operating costs for these range from 3-6 $/1,000 gallons. If the cost of the scrubbing water at 79 cents (?) per 1,000 gallons is significant enough to be included in the cost equations, then certainly the 3-6 $/1,000 gallons cost for disposing of the resultant brine should be included also.

IV. Contacts for Questions

If the EPA has questions about any of our comments the TCC will be glad to try to answer them; contact A. H. Nickolaus or J. B. Cox in care of the Texas Chemical Council, 1000 Brazos, Suite 200, Austin, Texas 78701. We can be reached by phone: A. H. Nickolaus, 512/572-1277 (Du Pont - Victoria, Texas) and J. B. Cox, 713/425-1046 (Exxon Chemical - Baytown, Texas).

AHN

References

1. EPA Docket No. A-81-25, Proposed NSPS for Air Oxidation Unit Processes, 48 FR 48932, October, 21, 1983.

2. Radian Corp. Report Prepared for Texas Air Control Board, "Assessment of the Feasibility and Costs of Controlling VOC Emissions from Stationary Sources in Harris County, Texas," July 29, 1981.

3. Reference 1, page 48942.

4. TCC Comments on Reference 1, Letter from A. H. Nickolaus (TCC) to Central Docket Section (A-130) dated December 22, 1983.

5. "Additional TCC Comments on the Draft Proposed NSPS for Polypropylene, Polyethylene, Polystyrene, and Poly (Ethylene Terephtlate) Manufacture" Letter from A. H. Nickolaus (TCC) to Jack R. Farmer (EPA) dated June 24, 1983.

6. Letter: A. H. Nickolaus (TCC) to Central Docket Section (LE-131), "Proposed NSPS for VOC Emissions from the SOCMI Distillation Unit Operations," March 9, 1984.

7. Peters, Max S. and Timmerhaus, Klaus D., "Plant Design and Economics for Chemical Engineers," Third Edition, Page 172-174, McGraw-Hill (1980).

8. Polymer Manufacturing Industry - BID for Proposed Standards, Preliminary Draft, EPA, March, 1983, Table 8-3.

9. VOC Fugitive Emissions in Petroleum Refining Industry - BID, Preliminary Draft, EPA, April, 1981, Table 8-5.

10. Blackburn, J. W. (I. T. Enviroscience) "Control Device Evaluation," July, 1980, EPA-450/3-80-026.

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4/84

TABLE 1

ANNUALIZED COSTS FOR AN EXAMPLE VENT STREAM

Stream: 284 SCM/Min. (10,000 SCFM)
0.37 MJ/SCM (10 BTU SCF)
76.1 Kg/Hour VOC Emissions
No Chlorinated Compounds in the Off-gas
June, 1980 Dollars

	EPA Estimate	TCC Estimate	Notes
Investment, 1,000 $	1,718	1,976	1
Labor Rates, $/Hour	11.10	18.00	2
Annual Costs, 1,000 $			
• Operations			
Labor, 2,133 Hours	23.68	38.39	3
• Maintenance			
Labor & Supplies, 3% Investment	51.54	59.28	4
Materials, 3% Investment	51.54	59.28	4
• Utilities			
Electricity, .049 $/KWH	12.30	12.30	
Natural Gas	66.10	156.15	5
Operating Supplies, 15% Maintenance	0	17.78	6
Engineering, Environmental Laboratory Analysis, and General Plant Overhead	0	39.07	7
Taxes @ 5% Investment	85.90	98.80	
Capital Recovery, 16.3% Investment	280.03	322.09	
Total, 1,000 $	519.55	803.14	

Notes:

1. Calculated for Category B per Table 5.5 in CTG. Investment in TCC estimate has been increased by 15% to partly allow for omitted items in EPA's estimate.

2. EPA labor rate from CTG Table 5-7. TCC rate from References 8 and 9 where $18.00 per hour "includes wages plus 40 percent for labor related administrative and overhead costs" (underlining added).

3. We presume the operating labor man-hours of 2,133 man-hour/year from Table 5-7 include an allowance for direct supervision as was done in Reference 8.

4. Maintenance labor plus materials factor of 6% split 50/50 between labor and materials. See Reference 7, page 201.

5. Intrastate natural gas in Texas in 1980 was about $2.60/MMBTU but by 1983 had increased to nearly $4.00, an increase of about 50% while overall costs increased about 20%. Since energy costs are still expected to increase faster than the general economy the $5.67/GJ ($5.98/MMBTU) cost factor from Reference 8, Table 8-3 has been used here for the TCC calculation. $2.40/GJ was used for the EPA estimate per CTG Table 5-7. These rates were used to calculate electrical and natural gas costs per formulas on CTG page E-5.

6. Taken as 15% of maintenance labor and materials per Reference 7, page 201.

7. Per the discussion under Section C2 above, these have been taken as 40% of operating plus maintenance labor.

AHN
4/84

UNION CARBIDE

UNION CARBIDE CORPORATION
ETHYLENE OXIDE/GLYCOL DIVISION
P.O. BOX 8361, SOUTH CHARLESTON, WEST VIRGINIA 25303

April 23, 1984

Mr. Robert Rosensteel
U.S. Environmental Protection Agency
North Carolina Mutual Building
411 W. Chapel Hill Street (Room 730)
Durham, N.C. 27701

Mr. Rosensteel:

Union Carbide Corporation, a major producer of synthetic organic chemicals by air oxidation processes, submits the attached comments on EPA's draft control technology guideline (CTG) document for control of volatile organic compound emissions from air oxidation processes in the synthetic organic chemical manufacturing industry.

Our submission of these comments has been delayed several days beyond the official April 19 due-date because the draft CTG was not available from the EPA until a short time before that date. (My copy of the document arrived with less than a week remaining.) When I called you on April 19, you said that comments would be considered as long as they were mailed within about a week after April 19.

We would welcome the opportunity to discuss these comments with you. If you have any questions, please call me (304) 747-2346.

Very truly yours,

Dennis C. Macauley /jgh

D. C. Macauley
Environmental Affairs Manager

DCM/jgh/0642B,D20B

Attachment

UNION CARBIDE CORPORATION

COMMENTS ON "EPA'S" DRAFT "CTG" DOCUMENT FOR CONTROL OF VOLATILE ORGANIC COMPOUND EMISSIONS FROM AIR OXIDATION PROCESSES

1. We note wording on pages 4-1 and 4-2 that places restrictions on what constitutes a proper point in an existing process unit for defining the VOC content of the emissions. While we can see that an effort has been made in the text to define the emissions point in a fairly broad way, it seems logical to us to broaden the definition still further. Simply stated, it seems logical that the evaluation of the cost for effecting a further reduction in emissions should start with what is actually being emitted by the existing facility, regardless whether the last step in the process is a) product recovery, b) energy recovery, or c) even a less-than-ideal (but already existing) emissions control device.

2. We feel that the RACT recommended in Chapter 4 does not adequately consider and make provision for use of catalytic oxidation as an alternative to thermal oxidation for emissions control. We ask that clarifying additions be made to supply state agencies with accurate and appropriate guidance in this regard and that overly restrictive criteria be relaxed.

   We find no fault with the preceding discussion in Chapter 3 - Emission Control Techniques, inasmuch as it:

   a. Cited catalytic oxidation as the second most common form of emissions control for an oxidation process.

   b. Properly described the role of catalytic oxidation under pressure as a means of enhancing energy recovery.

   c. Properly defined the range of reduction efficiencies for catalytic oxidation.

   The problem lies in the RACT itself, where the alternatives to meeting the TRE criterion are only a) a reduction efficiency of 98% (presumably based on the existing emissions rate) or b) reduction of VOC to 20 ppm. The text on page 4-1 is somewhat ambiguous in regard to these alternative criteria of 98% reduction or 20 ppm. However, their treatment as criteria is brought out quite explicitly on pages E-14 and E-15.

   We strongly question the apparent premise for these restrictions, namely that thermal oxidation is the only technology that is universally applicable. The text on page 4-1 includes a statement that the "RACT recommendation itself would not specify thermal oxidation as the only VOC control method." In light of that statement, we are puzzled by the restrictions nevertheless imposed by the criteria. These criteria, as Chapter 3 points out, can be met only by thermal oxidation.

As we have emphasized earlier in commenting on the NSPS, our concern is that proper cognizance is not being taken of the cost effectiveness of catalytic oxidation, where it is applicable. The cost advantages accrue from reduced (or even zero) requirements for supplementary air and/or fuel and from lower investment and operational attention.

Accordingly, we urge that the RACT criteria be modified in appropriate conformance with the text in Chapter 3.

Other comments that we wish to bring to the Agency's attention involve errors or inconsistencies.

1. Printing errors on pages 3-18, 3-19, and 3-20 have resulted in the omission of one portion of the text and the duplication of other portions.

2. Even though the TRE formula and the table of coefficients in the CTG appear to be identical with the formula and coefficients in the BID for the NSPS, there is an inconsistency in the monetary definition of the index.

   a. The CTG defines a TRE Index of 1.0 as corresponding to $1600/Mg destroyed.

   b. The BID for the NSPS specifies a value of $886.60 for a TRE Index of 1.0. (This $886.60 value, incidentally, corresponds to the value of $1900 for a TRE Index of 2.2 that is cited in the preamble of the published standards.)

   We are puzzled as to how such divergent values can result from what appears to be the same formula and set of coefficients.

3. We also fail to detect in the table of coefficients the changes we would expect to see as a result of the retrofit factor of 1.625 that is discussed earlier in the text.

   (The thought strikes us that perhaps the wrong table of coefficients has been printed in the CTG report. However, if that is the case, the example in the appendix is also in error.)

RAH:AWB/jgh/0642B,D20

APPENDIX H: REFERENCE METHODS AND PROCEDURES

APPENDIX H. REFERENCE METHODS AND PROCEDURES

H.1 INTRODUCTION

This appendix presents the reference methods and procedures recommended for implementing RACT. Methods and procedures are identified for two types of RACT implementation: (1) determination of VOC destruction efficiency for evaluating compliance with the 98-weight percent VOC reduction or 20 ppmv emission limit specified in the recommended RACT; and (2) determination of offgas flowrate, hourly emissions, and stream net heating value for calculating a TRE index. All reference methods identified in this appendix refer to the reference methods specified at 40 CFR Part 60 - Appendix A.

H.2 VOC DESTRUCTION EFFICIENCY DETERMINATION

(a) The following reference methods and procedures are recommended for determining compliance with the percent destruction efficiency specified in the recommended RACT.

(1) Reference Method 1 or 1A, as appropriate, for selection of the sampling site. The control device inlet sampling site for determination of vent stream molar composition or total organic compound destruction efficiency shall be prior to the inlet of any control device and after all recovery devices.

(2) Reference Method 2, 2A, 2C, or 2D as appropriate, for determination of the volumetric flowrate.

(3) Reference Method 3 to measure oxygen concentration for the air dilution correction. The emission sample shall be corrected to 3 percent oxygen.

(4) Reference Method 18 to determine the concentration of total organic compounds (minus methane and ethane) in the control device outlet and total organic compound reduction efficiency of the control device.

H.3 TRE INDEX DETERMINATION

(b) The following reference methods and procedures are recommended for determining the offgas flowrate, hourly emissions, and the net heating value of the gas combusted to calculate the vent stream TRE index value.

(1) Reference Method 1 or 1A, as appropriate, for selection of the sampling site. The sampling site for the vent stream flowrate and molar composition determination prescribed in (b)(2) and (3) shall be prior to the inlet of any combustion device, prior to any post-reactor dilution of the stream with air, and prior to any post-reactor introduction of halogenated compounds into the vent stream. Subject to the preceding restrictions on the sampling site, it shall be after the final recovery device. If any gas stream other than the air oxidation vent stream is normally conducted through the recovery system of the affected facility, such stream shall be rerouted or turned off while the vent stream is sampled, but shall be routed normally prior to the measuring of the initial value of the monitored parameter(s) for determining compliance with the recommended RACT. If the air oxidation vent stream is normally routed through any equipment which is not a part of the air oxidation facility as defined in Chapter 4, such equipment shall be

bypassed by the vent stream while the vent stream is sampled, but shall not be bypassed during the measurement of the initial value of the monitored parameter(s) for determining compliance with the recommended RACT.

(2) The molar composition of the vent stream shall be determined as follows:

(i) Reference Method 18 to measure the concentration of all organics, including those containing halogens.

(ii) ASTM D1946-67 (reapproved 1977) to measure the concentration of carbon monoxide and hydrogen.

(iii) Reference Method 4 to measure the content of water vapor, if necessary.

(3) The volumetric flowrate shall be determined using Reference Method 2, 2A, 2C, or 2D, as appropriate.

(4) The net heating value of the vent stream shall be calculated using the following equation:

$$H_T = K_1 \sum_{i=1}^{n} C_i H_i$$

where: H_T = Net heating value of the sample, MJ/scm, where the net enthalpy per mole of offgas is based on combustion at 25°C and 760 mm Hg, but the standard temperature for determining the volume corresponding to one mole is 20°C, as in the definition of Q_s (offgas flowrate).

K_1 = Constant, $1.740 \times 10^{-7} \left(\frac{1}{\text{ppm}}\right) \left(\frac{\text{g mole}}{\text{scm}}\right) \left(\frac{\text{MJ}}{\text{kcal}}\right)$,

where standard temperature for g-mole/scm is 20°C.

C_i = Concentration of sample component i, ppm, as measured by Reference Method 18 and ASTM D1946-67 (reapproved 1977), reported on a wet basis.

H_i = Net heat of combustion of sample component i, kcal/g-mole based on combustion at 25°C and 760 mm Hg. The heats of combustion of vent stream components would be required to be determined using ASTM D2382-76 if published values are not available or cannot be calculated.

(5) The emission rate of total organic compounds in the process vent stream shall be calculated using the following equation:

$$E_{TOC} = K_2 \left(\sum_{i=1}^{n} C_i M_i \right) Q_s$$

where: E_{TOC} = TOC emission rate of total organic compounds (minus methane and ethane) in the sample, kg/hr.

K_2 = Constant, 2.494×10^{-6} (1/ppm)(g-mole/scm) (kg/g)(min/hr), where standard temperature for (g-mole/scm) is 20°C.

M_i = Molecular weight of sample component i, g/g-mole.

Q_s = Vent stream flowrate (scm/min), at a standard temperature of 20°C.

(6) The total vent stream concentration (by volume) of compounds containing halogens (ppmv, by compound) shall be summed from the individual concentrations of compounds containing halogens which were measured by Reference Method 18.

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
Office of Air Quality Planning and Standards
Research Triangle Park, North Carolina 27711

February 4, 1985

Dear Sir or Madam:

Enclosed is a copy of the final control techniques guideline document, "Guideline Series - Control of Volatile Organic Compound (VOC) Emissions from Air Oxidation Processes in Synthetic Organic Chemical Manufacturing Industry." This document defines reasonably available control technology for VOC emissions from air oxidation processes. It was developed to assist States that have been granted extensions beyond December 31, 1982, to demonstrate attainment with the national ambient air quality standard for ozone.

A Federal Register notice announcing the availability of the final document is also enclosed. Copies of the document are being distributed to those who requested the draft documents and other interested parties.

Sincerely,

Susan R. Wyatt

Susan R. Wyatt, Chief
Chemicals and Petroleum Branch
Emission Standards and
Engineering Division

2 Enclosures

[AD-FRL-2744-6]

Control Techniques Guideline Document VOC Emissions From Air Oxidation Processes in the Synthetic Organic Chemical Manufacturing Industry

AGENCY: Environmental Protection Agency (EPA).

ACTION: Notice of availability of final control techniques guideline (CTG) document.

SUMMARY: The final CTG document for control of volatile organic compound (VOC) emissions from air oxidation processes in the synthetic organic chemical manufacturing industry (SOCMI) is available. This document provides guidance to States in determining reasonably available control technology (RACT) for VOC emissions from air oxidation processes.

ADDRESSES: Copies of the final CTG document may be obtained by contacting the Environmental Research Library (MD-35), (919) 541-2777, Environmental Protection Agency, Research Triangle Park, North Carolina 27711. Please refer to "Guideline Series—Control of Volatile Organic Compound Emissions from Air Oxidation Processes in Synthetic Organic Chemical Manufacturing Industry, EPA-450/3-84-015. Comments received on the draft CTG document are attached as an appendix to the final CTG document and are also availale for public inspection and copying between 8:30 a.m. and 4:00 p.m., Monday through Friday, at the Chemicals and Petroleum Branch, Room 730, Environmental Protection Agency, 411 West Chapel Hill Street, Durham, North Carolina.

FOR FURTHER INFORMATION CONTACT: Mr. Robert E. Rosensteel, (919) 541-5671, Chemicals and Petroleum Branch (MD-13), Emission Standards and Engineering Division, Environmental Protection Agency, Research Triangle Park, North Carolina 27711.

SUPPLEMENTARY INFORMATION: On March 5, 1984 (49 FR 8077), the EPA announced the availability for public review of the draft CTG document for VOC emissions from air oxidation processes in the synthetic organic chemical manufacturing industry. The CTG document presents the Agency recommendation of reasonably available control technology (RACT) requirements for air oxidation processes. The recommended RACT has not changed since the draft CTG was published for comment. In general, the recommended RACT would require certain affected air oxidation facilities to reduce VOC emissions by 98 weight percent or to 20 parts per million by volume (ppmv), whichever is less stringent. The air oxidation facilities requiring such VOC emission reductions would be those that are below a cost-effectiveness cutoff level expressed as a total resource effectiveness (TRE) index value of 1.0.

Air oxidation processes are present in synthetic organic chemical manufacturing plants and include all reactions in which air, or air enriched with oxygen, is the oxidizing agent. There are 36 or more chemicals made by the air oxidation process. A common feature of air oxidation processes is that they all involve venting large quantities of nitrogen gases containing VOC to the atmosphere. However, the quantity of VOC emissions and both the overall cost and cost effectiveness of control very considerably depending on the chemical and the process. Total resource effectiveness or "TRE" is a measure of the cost effectiveness of controlling air oxidation streams with a 98 percent efficient combustion device (thermal oxidation). An equation for estimating the TRE value for individual vent streams from air oxidation facilities is included in the RACT recommendation. The equation, which is described in the CTG document, incorporates several vent stream characteristics that affect cost effectiveness. These include flowrate, hourly VOC emissions, corrosive properties, and net heating value. The TRE equation is not affected by inflation. A TRE index of 1.0 is equivalent to a cost effectiveness of $1,600/Mg (1980 dollars) of VOC emission reduction. Thus, for facilities with a process vent steam or combination of process vent streams having a TRE index value that exceeds the recommended cutoff level of 1.0 (equivalent to $1,600/Mg), a 98 percent VOC emissions reduction is not required. Air oxidation processes that already are controlled by combustion devices would not have to meet the 98 percent requirement until the combustion device is replaced for other reasons; in other words it is recommended that no plant be required to upgrade or replace an existing combustion device.

Six comment letters were received from industry representatives and trade groups as a result of the EPA request. All comments contained in these letters were considered before the final CTG document was prepared, and responses to these comments were provided in Appendix F. Many comments were received requesting clarifications on the applicability of the RACT requirements. These clarifications have been added in Appendix F.

Several commenters suggested that the RACT requirements be relaxed by lowering the $1,600/Mg cost-effectiveness cutoff used to determine whether VOC emissions would have to be reduced by 98 percent or to 20 ppmv. However, the RACT requirements were not changed. It is not likely that any facility will actually incur a cost effectiveness near the $1,600/Mg level. The reasons for this are (a) Less expensive combustion control techniques are likely to be used, thus reducing the costs and cost effectiveness incurred by individual facilities, and (b) relatively less expensive product recovery devices may be used to decrease emissions and thus raise TRE values above the cutoff so that VOC emissions would not have to be reduced by 98 percent or to 20 ppmv. The RACT cutoff was established assuming that thermal incinerators will be used to reduce VOC emissions by 98 weight percent. However, many facilities will opt to use boilers, process heaters, flares, or catalytic oxidizers. When these devices are used, the costs of control will be significantly reduced over the cost of thermal incineration. Furthermore, the RACT requirements do not require VOC emissions to be reduced by 98 percent if a TRE index greater than 1.0 is maintained. The EPA believes that some facilities having a TRE index below the 1.0 cutoff (equivalent to $1,600/Mg) will upgrade product recovery to reduce VOC and raise their TRE values above 1.0. This will also significantly reduce the costs of control incurred by the industry. To study the potential impacts of requiring air oxidation facilities to control VOC emissions using thermal incinerators, the Agency developed a statistical profile of facilities which is assumed to represent all existing air oxidation facilities. An analysis of these facilities indicated that the maximum cost effectiveness incurred by any facility in the statistical profile required to reduce VOC emissions by 98 percent or to 20 ppmv would be about $1,000/Mg. This analysis shows that facilities in the statistical profile with cost-effectiveness values greater than $1,000/Mg would be able to upgrade product recovery to achieve a TRE greater than 1.0.

Two commenters requested that the requirements be changed so that combustion by catalytic oxidation can be used. One commenter contended that a catalytic oxidizer at his plant achieves only 95 percent control. In fact, the recommended RACT would not require replacement of this existing combustion device to achieve the 98 percent requirement. However, studies performed by the EPA Office of Research and Development indicate that a catalytic oxidation device applied to a stream very similar to the stream at the commenter's facility can achieve a VOC destruction efficiency of 98 percent.

Several comments were received claiming that incinerator costs were underestimated and the TRE equation was not accurately predicting the cost-effectiveness values for facilities. The commenters suggested that additional equipment needed to be added to the algorithms and some cost factors needed to be revised. Upon evaluating these comments, several revisions were made to ensure that the algorithms would predict costs that are representative of the costs that will be incurred by most air oxidation facilities. The items that were changed included ductwork length, natural gas price, labor factors, and other utility factors.

The CTG document is part of the third group of CTG documents published to assist the States in determining RACT for various stationary sources of VOC emissions. These documents provide State and local air pollution control agencies with an initial information base for proceeding with their own analysis of RACT for specific source categories of VOC emissions located within areas where an extension was granted for the attainment of the national ambient air quality standard for ozone. The CTG documents review existing information and data concerning the technology and cost of various control techniques to reduce VOC emissions.

This CTG is not a "rule" as defined by the Administrative Procedure Act (5 U.S.C. 551 et seq.). It is a "rule" for purposes of Executive Order 12291 because it is designed to implement an EPA policy. Under Executive Order 12291, the EPA must judge whether a rule is "major" and, therefore, subject to the requirements of a regulatory impact analysis. The CTG documents are not "major rules" because they do not impose any new requirements. This notice and the final CTG document were submitted to the Office of Management and Budget (OMB) for review. Any comments from the OMB to the EPA and any EPA responses to those comments are available for public inspection.

Dated: November 26, 1984.

John C. Topping,

Acting Assistant Administrator for Air and Radiation.

[FR Doc. 84-33757 Filed 12-27-84; 8:45 am]

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